PETROLEUM RECOVERY INSTITUTE

THE RHEOLOGY OF HEAVY OILS AND WATER-IN-HEAVY OIL EMULSIONS

FINAL REPORT

BY

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CALGARY, ALBERTA

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EXECUTIVE SUMMARY

This report presents results of a cost-shared investigation of the rheological properties of water-in-heavy oil emulsions. The investigation started with a review of the literature on oil field emulsions. Available information on the forces affecting stability of emulsions was reviewed first. It was found that interfacial films play an important role in stabilizing water-in-heavy oil emulsions. The rheology of emulsions containing only a small fraction of dispersed phase (< 10 vol percent) appears to be reasonably well understood. However, the rheological behaviour of concentrated emulsions (dispersed phase >30 %) is very complex and difficult to analyze theoretically. Effect of several factors, such as droplet size distribution, viscosity ratios of the continuous phase and dispersed phase, and interfacial viscosity of the adsorbed films, is not fully known. Therefore, for engineering applications, phenomenological models based on macroscopic behaviour of emulsions appear to be more promising at present.

A rheometer capable of operating at high temperatures (up to 200°C) and moderate pressures (up to 3.5 MPa.) was assembled and rheological properties of several water-in-heavy oil emulsions were measured.

SOMMAIRE

Cet exposé presente les résultats d'une étude, à coûts partagés, sur les propriétés rhéologiques de certaines émulsions eau-huiles lourdes. L'étude commenca par une recherche litéraire sur les émulsions pétrolifères. La litérature déjà existante, sur les forces affectants la stabilitée dés émulsions, fut examinée en premier lieu. Ainsi, l'on trouva que les pellicules d'interface jouent un rôle important dans la stabilitée des émulsions eau-huiles lourdes. La rhéologie des émulsions contenant une petite fraction de la phase dispersée (<10 % Vol.), semble être bien comprise. Cependant, le comportement rhéologique d'emulsions concentrés (phase dispersee >30 %), est très complexe et difficile à analyser théoriquement. Plusieurs paramêtres tel que, la distribution de la grosseure des gouttelettes, le rapport de viscosité entre la phase principale et la phase dispersée ainsi que la viscosité d'interface des pellicules absorbées, ne sont pas entièrement connus. Donc, pour les applications d'ingenierie, les modeles empiriques basés sur le comportement macroscopique semblent être prometteurs.

Un rheomêtre, capable de fonctionner à haute température (jusqu'a 200 deg. C), ainsi que des pressions dites moyennes (jusqu'a 3.5 MPa), fut mis au point. Par la suite, on pu mesurer les propriétées rhéologiques de plusieurs émulsions eau-huiles lourdes.

1: INTRODUCTION

Crude oils, found in underground reservoirs, are almost always associated with formation brine and gas. Often large quantities of water are co-produced with the oil. As a consequence, a large fraction of the crude oil produced contains emulsified water. This is especially true of heavy oils. In primary production, the source of water for the emulsion is the connate water in the formation. In secondary and tertiary recovery, the water co-produced with oil may also originate from injection wells. Oil field emulsions generally occur as water droplets dispersed in oil (W/O) and occasionally as oil droplets dispersed in water (O/W). In addition, sometimes they may exist as double or multiple macroemulsions in the form of water droplets dispersed in oil droplets which are dispersed in the continuous water phase (W/O/W) or oil droplets dispersed in water droplets which are dispersed in the continuous oil phase (O/W/O).

While it has been claimed that emulsions are produced when the constituents move through valves and other flow constrictions which produce high shear stress, it is also known both from theoretical and experimental considerations that emulsions can be formed in the reservoir (Uzoigwe and Marsden, 1970). Reservoir parameters such as porosity, temperature, type of crude oil, gas-oil-water ratios, and production parameters such as well depth and type of completion can affect emulsion formation (Lissant, 1977).

In addition, the use of high viscosity emulsions to displace heavy oils as a secondary recovery scheme has been suggested (Farouq Ali et al., 1979; Fiori, 1983; Nasr et al., 1988). Emulsions have been proposed as blocking agents in steam flooding (Decker and Flock, 1988), as viscous fluids during

fracturing operations (Sinclair, 1970), and as means of transportation of heavy oils through pipelines (Marsden and Rose, 1971; Plegue et al., 1986).

Emulsion theory has developed in the fields such as chemistry and pharmacy where components used are either pure or of known composition. Moreover, the components are usually chosen so that the viscosity does not cause any major problems during the emulsion stability and rheology studies, or during emulsification. There has been a considerable amount of work done in the area of microemulsion (droplet size < 1 micron); whereas relatively little work has been done in the area of macroemulsion (droplet size > 1 micron). Mostly O/W emulsions were studied while, as it was stated, a large portion of the crude oil is produced as W/O macroemulsion. However, little experimental information exists for complex crude oil systems (Jones et al., 1978). There have been relatively few studies of the factors which influence the rheological properties of emulsions, in contrast to the large number of detailed studies on dispersions of solid particles (Sherman, 1983).

This report presents the results of an investigation into the rheological properties of water-in-heavy oil emulsions. A review of the literature on oil field emulsions is presented in the next chapter. The experimental apparatus developed for measuring rheological properties of water-in-heavy oil emulsions is discussed in Chapter 3. Chapter 4 presents the results of these measurements. The last chapter discusses the implications of these results for heavy oil production and identifies areas in which further research is needed.

2: LITERATURE REVIEW

The available literature on oil field emulsions was reviewed to define the state of the art in this area. It was found that oil-in-water type emulsions have been studied more extensively. The topics which have been of primary interest to the oil industry are the emulsion stability and the emulsion breaking process. The factors affecting emulsion stability and ways of breaking the emulsions appear to be well understood. Rheology of emulsions has also been investigated but is not so well understood. A summary of what the literature review found follows.

2.1 STABILITY OF EMULSIONS

An emulsion is a thermodynamically unstable system and possesses a natural tendency to separate into two phases. With the dispersion of one phase into another, the interfacial area is greatly increased as is the free energy of the interface which is proportional to the interfacial area. Therefore any oil-water system tends to minimize this free energy by reducing the size of the contact area and by inducing coalescence of the dispersed droplets. This result may be prevented by stabilizing agents which are either added or naturally occurring.

2.1.1 STABILIZING AGENTS

Four classes of stabilizing agents can be distinguished (Kitchener and Musselwhite, 1968): First, and the least effective, are certain types of inorganic electrolytes which are used to stabilize O/W emulsions. The stabilization is due to the formation of double layers on the aqueous side of

the interface as a result of preferential adsorption of one type of ion. The long range forces of repulsion between electrical double layers keep droplets apart. A second class comprises the highly surface-active compounds of soaps and detergents. They are constituted of a hydrocarbon portion and a polar or ionic portion. The hydrocarbon portion, which can be linear or branched, interacts very weakly with water molecules in the aqueous environment. Hence this chain is usually called hydrophobic. The polar or ionic portion, on the other hand, interacts strongly with the water via dipole-dipole or ion-dipole interactions and is solvated. Consequently, it is said to be hydrophilic. Surface active agents are generally classified depending on the nature of the hydrophilic group, that is, anionic, cationic, nonionic or zwitterionic (Ottewill, 1984). The unique property of these materials is their ability to absorb strongly at the oil-water interface and to lower the interfacial surface energy.

Furthermore ionic surfactants, like polyelectrolytes, promote a charge stabilization mechanisms whereas nonionic surfactants gives rise to a steric stabilization mechanism (Tadros and Vincent, 1983). At equilibrium, the adsorbed nonionic surfactant forms an adsorbed layer comprised of loops and tails extending into the solution phase. When two droplets approach each other, a repulsive force is generated owing to the presence of these adsorbed layers. This stabilizing effect is usually referred to as steric stabilization.

Still greater stability can be achieved with the third class of stabilizing agent which are macromolecular emulsifying agents such as certain proteins, gums, starches and polymers. The stabilization of such emulsions has been attributed to formation of tough skins formed at the interface. The

adsorption of macromolecules at the liquid/liquid interface is a slow process which is practically irreversible and gives rise to a steric mechanism of stabilization. Moreover, the macromolecular film formed at the oil-water interface can, in view of its viscoelastic properties, in certain circumstances provide a mechanical barrier to coalescence. This is particularly the case with many oil field emulsions (Reisberg and Doscher, 1956; Blair, 1959; Kimbler et al., 1966; Strassner, 1968; Uzoigwe and Marsden, 1979; MacKay et al., 1973; Jones et al., 1978; Neustadter et al., 1981; Mukherjee and Kushnick, 1988). Properties of these films and their effect on emulsion rheology will be discussed in detail later.

Finally, the fourth class of emulsifying agent comprises finely divided insoluble solids which stick to the interface by reason of surface tension forces. Once situated at the interface, the solid particles make coalescence of droplets more difficult, essentially by keeping the droplets from coming into close contact (Tadros and Vincent, 1983). In the case of oil field emulsions these solids may be formation fines, crystalline wax or asphaltene particles (Smith and Ramsden, 1978; Thompson et al., 1985; Stockwell et al., 1986; Eley et al., 1988a).

2.2 EMULSION BREAKING PROCESSES

Emulsion droplets of a particular size disappear by any of three processes: Brownian flocculation, sedimentation flocculation, and creaming (Reddy and Fogler, 1981). Brownian flocculation is due to the random thermal motion of droplets, creaming is due to the gravitational force on the particles, and sedimentation flocculation is due to different creaming velocities of different size droplets. All the loss processes are due to

thermal and gravitational forces, provided that there is no external force field. If gravitational forces are negligible, the droplets will disappear only by Brownian flocculation. Generally, if the droplets are very small or if the density of the droplets is nearly equal to the density of the medium, the gravitational forces will be negligible. Random thermal forces will be negligible on the larger droplets.

2.2.A. SEDIMENTATION AND CREAMING

The creaming and sedimentation processes occur in emulsion systems mainly due to the density difference between the dispersed and continuous phase. Assuming a steady-state is reached, the sedimentation or creaming velocity v of a uniform, non-deformable, noninteracting sphere of radius a in a liquid of viscosity μ_o is given by Stokes' law (Sharma and Shah, 1985)

$$v = \frac{2\ \Delta\rho\ g\ a^2}{9\ \mu_o} \qquad (1)$$

where $\Delta\rho$ is the density difference and g is the acceleration of gravity. Thus, particles of smaller diameter move slower and they will move faster in a less viscous fluid. The applicability of Equation (1) to emulsions depends on the validity assumptions involved in Stokes' law. With liquid droplets, the assumption of a smooth surface is reasonable, except perhaps when solid particles are present as stabilizers (Tadros and Vincent, 1983). A generally accepted rule is that gravitational force on the droplet can be neglected if the velocity given by Equation (1) is less than 1 mm/day (Reddy and Fogler, 1981).

The question of deformability is a more serious problem. A liquid droplet moving within a second liquid phase has an internal circulation

imparted to it. As a result of this motion, the new sedimentation or creaming velocity will be given by (Reddy and Fogler, 1981)

$$v = \frac{2\,\Delta\rho\,g\,a^2}{3\mu_o}\,\frac{\mu_o + \mu_i}{3\mu_o + 2\mu_i} \qquad (2)$$

where μ_i is the viscosity of the internal phase. For the case $\mu_i \gg \mu_o$ (O/W emulsions), Equation (2) predicts v to be 50% greater and for the case $\mu_i \ll \mu_o$ (W/O emulsions), v is predicted to be one third of that given by Stokes' law.

Another limitation to be considered in the application of Stokes' law is that it strictly applies only to non-interacting droplets, and thus it is only valid for very dilute emulsions. In most practical emulsions the droplet concentration is high. Moreover, there is a wide variation in droplet size. In this case, if there is no flocculation and coalescence, a velocity for the centre of the mass of the dispersed phase is given by

$$v = \sum_i \frac{8\pi\,g\,n_i\,a_i^5\,\Delta\rho}{27\mu_o\,V} \qquad (3)$$

where n_i is the number of droplets having a radius a_i and V is the total volume of the dispersed phase. It should be remembered that equation (3) involves the same assumptions and approximations as Equation (1).

2.2.B. FLOCCULATION

The maintenance of droplets in an emulsion as individual primary units and their combination to form secondary units such as aggregates, agglomerates, or flocs depends on the interaction of forces between them. A considerable amount of modern fundamental work on the theory of stability of

emulsions has been devoted to the question of how far the theory of colloid stability developed independently by Derjaguin and Landau, and by Vervey and Overbeek (DLVO theory) goes towards explaining properties of emulsions.

The DLVO theory is based on the concept that dispersed droplets are subject to long range London-van der Waals forces and electrostatic forces associated with the overlap of the electrical double layers around the charged droplets. When added together this leads to the total mutual interaction free energy which determines the chance that when two such droplets come together, under the influence of random Brownian motion, they will or will not come into close contact and remain in contact. Caution must be exercised in applying the theory to droplets stabilized by adsorbed emulsifying agents where certain modifications are necessary. Furthermore, the theory cannot be expected to apply to the rate of coalescence of emulsion droplets because this process depends on displacing or disrupting an adsorbed film. Nor can the theory be applied to emulsions stabilized by solid particles (Kitchener and Musselwhite, 1968).

1. Electrostatic Interactions:

Electrostatic interactions result when using ionic surfactants of the anionic, cationic and zwitterionic type as well as in the presence of electrolytes (Tadros, 1984). The surface charge may be caused either by ionization of the surface groups, by adsorption of ions onto the surface or by direct exchange with the fluid. In order to maintain electrical neutrality, this surface charge must be balanced by an equal number of counterions in the surrounding fluid. For example, the bitumen-water interface is negatively charged due to dissociation of carboxyl groups belonging to natural

surfactants in the bitumen (Takamura et al., 1987). The surface charge together with the counterions forms the electrical double layer.

When two droplets each carrying a diffuse double layer of counterions approach each other due to Brownian motion, repulsion results from the overlap of double layers. As a result of this interaction the free energy of the system increases, that is, the interaction of the double layers will give rise to a repulsion between the surfaces of droplets. For spherical droplets, the repulsive energy is given by the following approximate expression when the range of interaction is small compared with the particle radii

$$G_R = 2\pi\, a\, \epsilon_r\, \epsilon_o\, \psi_o^2 \ln[1 + \exp(-\kappa h)] \qquad (4)$$

where ϵ_r is the dielectric constant of the medium, ϵ_o is the permittivity of the free space, ψ_o is the surface potential, h is the surface to surface separation and κ is the reciprocal of the thickness of the electrical double layer, given by

$$\kappa = \left(\frac{2Z^2e^2C}{\epsilon_r\epsilon_o kT}\right)^{1/2} \qquad (5)$$

where z is the valency of the counterions, C the electrolyte concentration in the bulk solution, e the electronic charge, k the Boltzman constant and T the absolute temperature.

It is clear from Equation (4) that G_R depends on ψ_o, a and κ. The surface potential is determined by the number of surfactant ions adsorbed per unit area. The higher ψ_o, the higher the repulsion. On the other hand, G_R is reduced in magnitude by an increase in κ (i.e. increase in electrolyte concentration). Furthermore, G_R is positive as long as diffuse layers are of the same sign. If these layers are of the opposite sign, the G_R becomes

attractive (negative). This is the case, for example, when a dispersion stabilized by anionic surfactant is mixed with one stabilized by cationic surfactant.

In the case of emulsions, two factors must be considered before deciding whether Equation (4) is applicable. These factors are the possibility of distortion of droplets as they interact and the existence of diffuse layers within the droplets themselves. If the droplets are stabilized by double layer repulsion to some degree, then close approach will tend to produce flattening of the surfaces. The potential energy barrier opposing contact of the droplets will therefore be greater than calculated on the assumption of rigid spheres, the effective radius of curvature being increased inward. The existence of an internal diffuse layer neutralizes some of the surface charge and the surface potential is reduced. However, the repulsion between the droplets through the interaction of their extended double layers is otherwise unaffected by the existence of internal double layers (Kitchener and Musselwhite, 1968; Bechter, 1977)

2. The London-van der Waals Interaction

The dispersion (London) forces arise from charge fluctuations within a molecule associated with the motion of its electrons. Therefore, these forces can operate even between nonpolar molecules. The mutual attractive energy between two infitesimal volume elements dV_1 and dV_2 in the vacuum is given by

$$dG_A = \frac{\beta_1 \, q_1^2 \, dV_1 \, dV_2}{h^6} \qquad (6)$$

where β_1 is the interaction energy of a pair of molecules of the type 1 at 1 cm apart in a vacuum and q_1 is the number of molecules per cm^3 in substance 1.

The London forces between two molecules are of short range as dG_A is inversely proportional to the sixth power of their separation. However, the net force between them is of much longer range. The interaction energy between two finite spheres can be obtained by integrating Equation (6),

$$G_A = -\frac{\pi^2 q_1^2 \beta_1}{6}\left[\frac{2a^2}{R^2 - 4a^2} + \frac{2a^2}{R^2} + \ln\frac{R^2 - 4a^2}{R^2}\right] \tag{7}$$

where R is the distance between the centers. The constant $\pi^2 q_1 \beta_1$ is commonly represented by A and called the Hamaker constant.

The interaction energy of material 1 suspended in a continuous medium 2 will be smaller than that given by Equation (7) because of interaction between the molecules of the medium and between the particles and the medium. In this case, Hamaker's constant to be used in Equation (7) should be redefined as

$$A = [\ A_{11} - A_{22}\ ]^2 \tag{8}$$

it follows that the net value of A is always positive, hence, emulsion droplets are always subject to a London-van der Waals attraction.

It can be seen from Equation (7) that London-van der Waals interaction of emulsion droplets does not become significant until the distance between particles are quite small (Kitchener and Musselwhite, 1968). Therefore it is sufficient to take, for all practical purposes, a simple form of Equation (7) obtained by putting $H = R - 2a$ and $h \ll a$, i.e. for separations which are very small compared to the radius of spheres. The approximate formula is

$$G_A = -\frac{Aa}{12h} \tag{9}$$

In the presence of an adsorbed surfactant layer, the London-van der Waals interaction has to be further modified since the layer may have a Hamaker constant, A_{33}, which is different from that of the medium and/or the droplet. In this case (Vold, 1961),

$$G_A = \frac{1}{12}(A_{22} - A_{33})^2 \frac{a+\delta}{a} + (A_{33} - A_{11})^2 \frac{a}{R+2\delta} + \frac{4a(A_{22} - A_{33})(A_{33} - A_{11})(a+\delta)}{(R+\delta)(2a+\delta)} \quad (10)$$

where δ is the thickness of the adsorbed surfactant layer and R is the surface to surface separation of layers. For the case $A_{11} > A_{22}$ (true in most situations), the presence of a surfactant layer leads to a reduction in G_A when $A_{33} > A_{22}$. However, when $A_{33} < A_{22}$, the adsorbed layer results in a net increase in G_A. If the Hamaker constant of the surfactant layer is close to that of the dispersion medium ($A_{33} \simeq A_{22}$), the surfactant layer will act as a simple barrier preventing the close approach of droplets, which may thus be kept out of the range at which London-van der Waals forces become strong (see Equation (10)). A possible example is the stabilization of W/O emulsions by surfactants with a very long oil soluble section such as those found naturally in crude oils.

3. Steric Interactions:

Steric interactions result when long chain surfactants which form thick adsorbed layers are present. These interactions arise when using nonionic surfactants or macromolecular surfactants, as soon as the adsorbed layers interfere with each other. It has been shown that the repulsive forces arise from the loss of configurational entropy and from changes in enthalpy when the

stabilizing segments begin to interpenetrate and compress during the collision process (Neville and Hunter, 1974)

There are two contributions to steric interactions. The first contribution arises from the build-up of segment concentration in the interaction zone which leads to an increase in local osmotic pressure and free energy. This contribution to steric interaction is usually referred to as the osmotic mixing term, G_M. Clearly, G_M operates as soon as the adsorbed layers overlap, i.e. when $h < 2\delta$ (Figure 1). With further overlap, compression of the chains may occur and the configurational entropy of the chain is reduced since the total volume available to the chain is reduced. This is especially the case when $h < \delta$. This interaction is known as the volume restriction term, G_{VR}. Thus, the total steric interaction energy is given by (Tadros, 1984)

$$G_S = G_M + G_{VR} \tag{11}$$

For the case of adsorbed surfactant layers of uniform segment concentration in the adsorbed layer, simple expressions for G_M and G_{VR} can be derived (Tadros, 1984):

$$G_M = \frac{4kT\,\pi\,\phi_2^2}{3V_1}\,(0.5 - \chi)\,(\delta - h/2)^2\,(2a + 2\delta + h/2) \tag{12}$$

and, at low coverage

$$G_{VR} = N_S\,kT\,\theta_\alpha\,[1-(h/\delta)] \tag{13}$$

where ϕ_2 is the volume fraction of the surfactant in the adsorbed layer, V_1 is the volume of a solvent molecule, χ is the chain-solvent interaction

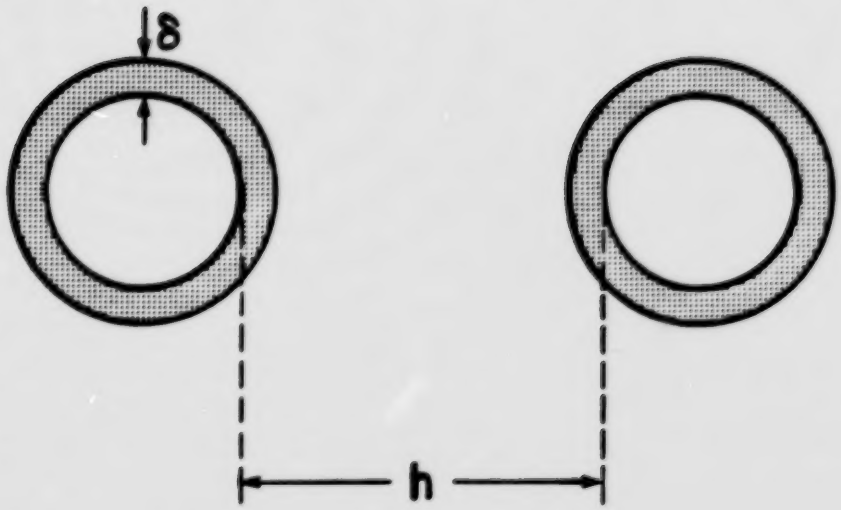

Figure 1- Droplets with adsorbed surfactant layers.

parameter, N_S is the number of adsorbed chains per unit area and θ_α is the fraction of surface covered by an adsorbed layer with the surfaces at infinite separation. It is clear from Equation (12) that G_M is positive as long as $\chi < 0.5$, i.e. the chains are under good solvent condition.

4. Total Interaction Free Energy and the State of the Emulsion:

The total interaction of droplets containing an adsorbed surfactant layer is given by

$$G_T = G_R + G_A + G_S \tag{14}$$

Two general cases may be considered, the first where there is little contribution from G_S, i.e. the case when ionic surfactants are present. In this situation G_T is given by the sum of G_R and G_A in the well known DLVO theory. A schematic representation of G_T as a function of distance of separation is shown in Figure 2 for this case.

This curve is characterized by a primary minimum G_{min} at close contact of droplets due to Born repulsion as a result of the overlap of electron shell at these distances; a maximum G_{max}, and a secondary minimum G_{min2} at large interdroplet separations. The magnitudes of G_{max}, G_{min} and G_{min2} are determined by the surface potential, electrolyte concentration, droplet size and Hamaker constant. Depending on the relative magnitude of the parameters, various states of the suspension are reached. For example, if G_{max} is much higher than the mean translational energy of colloidal particles ($G_{max} >> kT$) and G_{min2} is shallow, droplets must be stable against flocculation. That is, colliding droplets should bounce off one another without making contact and the emulsion should be stable, apart from creaming/sedimentation. This is the case when the surface change is high and electrolyte concentration is low.

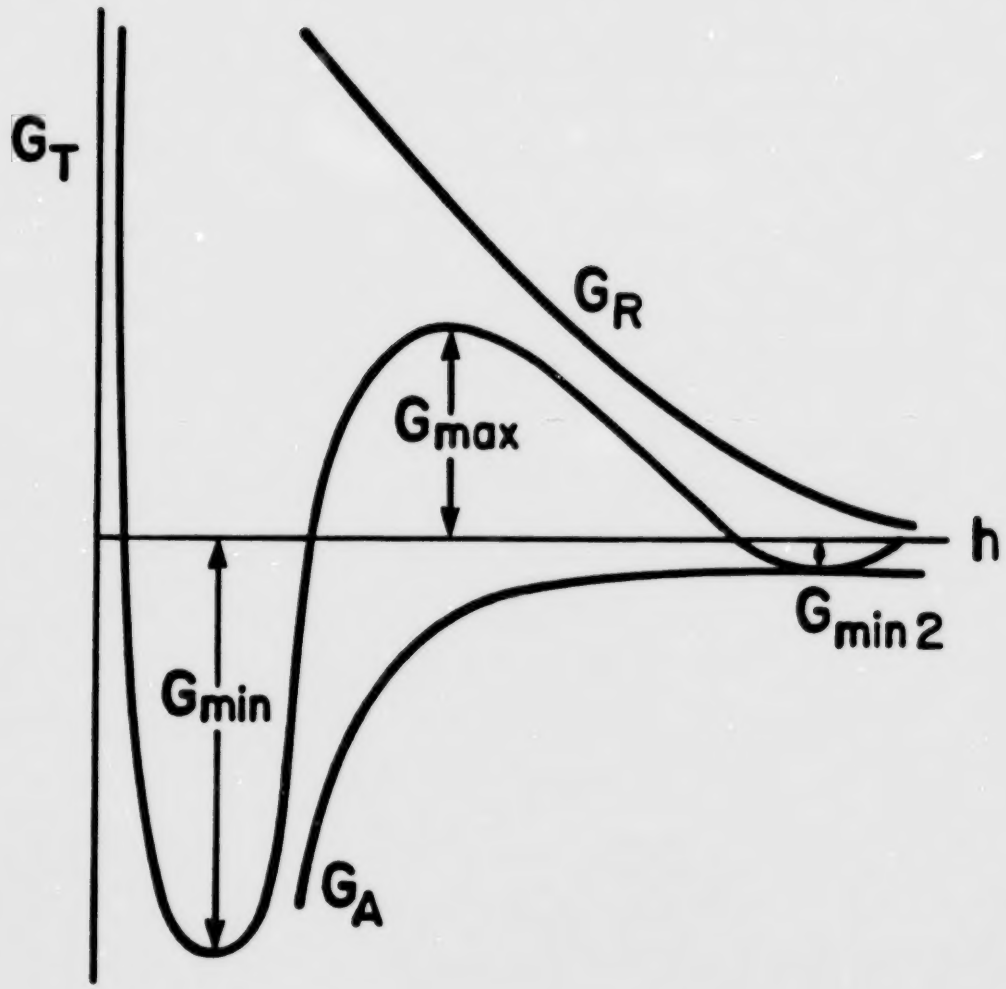

Figure 2 - Schematic representation of G_T according to DLVO theory.

If the surface potential is reduced and/or the ionic strength increased, the energy barrier G_{max} is lowered until it eventually becomes comparable in magnitude with kT, meaning that the dispersion should undergo slow flocculation. If there is no energy barrier ($G_{max} = 0$) then the droplets undergo rapid flocculation. Therefore, if G_{max} is small (<5-10 kT) or absent, the droplets are able to surmount the energy barrier and enter the deep primary minimum G_{min} and the suspension becomes coagulated. On the other hand, if G_{max} is reasonably large (>10 kT) and G_{min2} is fairly deep (1-5 kT), the droplets are held by relatively weak attraction at separation distances around the location of G_{min2}, and the emulsion becomes weakly flocculated. Under these circumstances, the emulsion may form a three-dimensional gel network structure, which can be fluidized by applying shear.

The second general case to consider is that in which there is a contribution from G_s as in the case of nonionic or macromolecular surfactants. Here, G_s dominates the interaction for $h < 2\delta$. At separation distances larger than 2δ, there is no contribution from G_s and the interaction is determined by G_R and G_A. The electrostatic interaction arises from the residual double layer interaction which is considerably modified by the presence of adsorbed layers. This electrostatic interaction becomes relatively unimportant when thick layers are present since it only operates at relatively small separation distances. Moreover, with thick adsorbed layers the contribution from G_A is also relatively small. Thus with systems containing adsorbed nonionic or macromolecular surfactant, G_T may be described in terms of G_S and G_A and the form of the energy distance curve is illustrated in Figure 3 which also shows various contributions (Tadros, 1984).

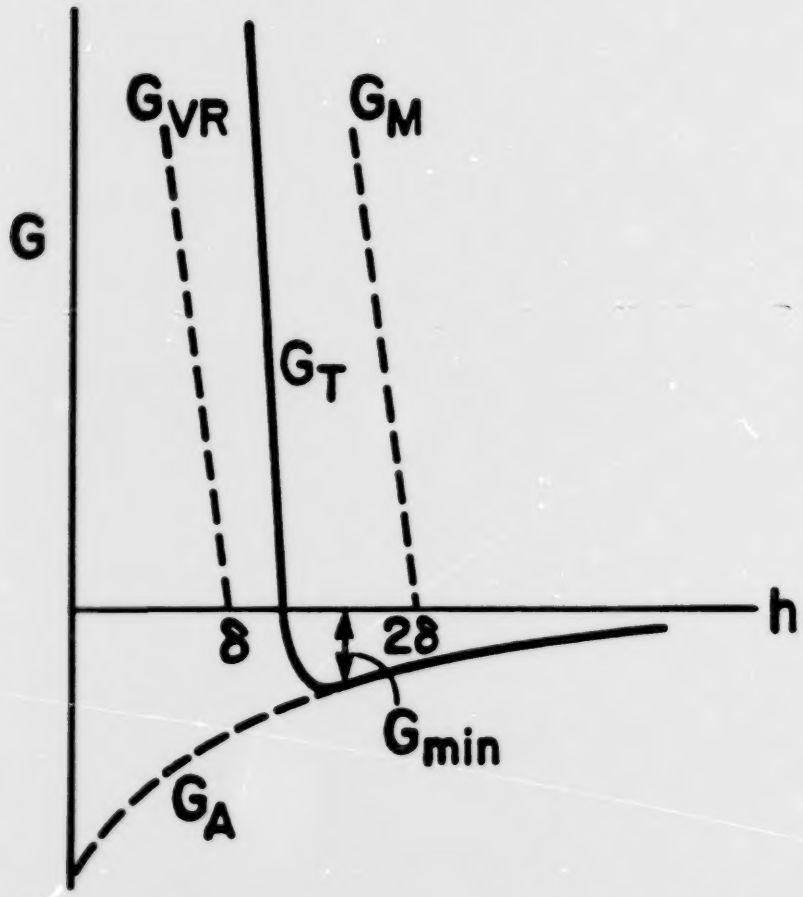

Figure 3 - Total interaction curve for sterically stabilized systems.

Unlike the DLVO type systems the energy-distance curve shows only one minimum, G_{min}, whose depth depends on the thickness of the adsorbed layer, droplet size and the Hamaker constant. When there is a thick adsorbed layer, G_{min} is shallow resulting in a highly stable emulsion as G_T shows a very sharp rise with reduction of h below 2δ. Thus, provided that the surfactant molecules are strongly adsorbed, steric stabilization offers a powerful means of producing a stable system.

As mentioned before, sterically stabilized emulsions can be destabilized by reducing the solvency of the chain to a point where $\chi \geq 0.5$(see Equation (13)). Under these conditions, G_M becomes negative and produces a deep minimum. This condition results in catastrophic flocculation of the emulsion.

5. **Application to W/O Emulsions**:

In systems in which water is the continuous phase, the thickness of the electrical double layer is generally about 10^{-3} to 10^{-2} microns so that electrical interactions take place only at very short distances (Albers and Overbeek, 1959a). The potential energy of the charged particles at a mutual distance of a few times 10^{-2} microns thus equals zero with regard to infinite distance as shown in Figure 2. Consequently, the total energy barrier G_{max} has to be crossed before flocculation can occur.

In systems in which a non-polar liquid such as oil is the continuous medium, the ionic concentration is extremely small and thus the thickness of the double layer can be about 10 microns (Hair and Landher, 1982; Albers and Overbeek, 1959b). This is shown in Figure 4. The thickness of the double layer is of the same order of magnitude as the distance between droplets in a moderately concentrated emulsion. The droplets therefore possess a potential

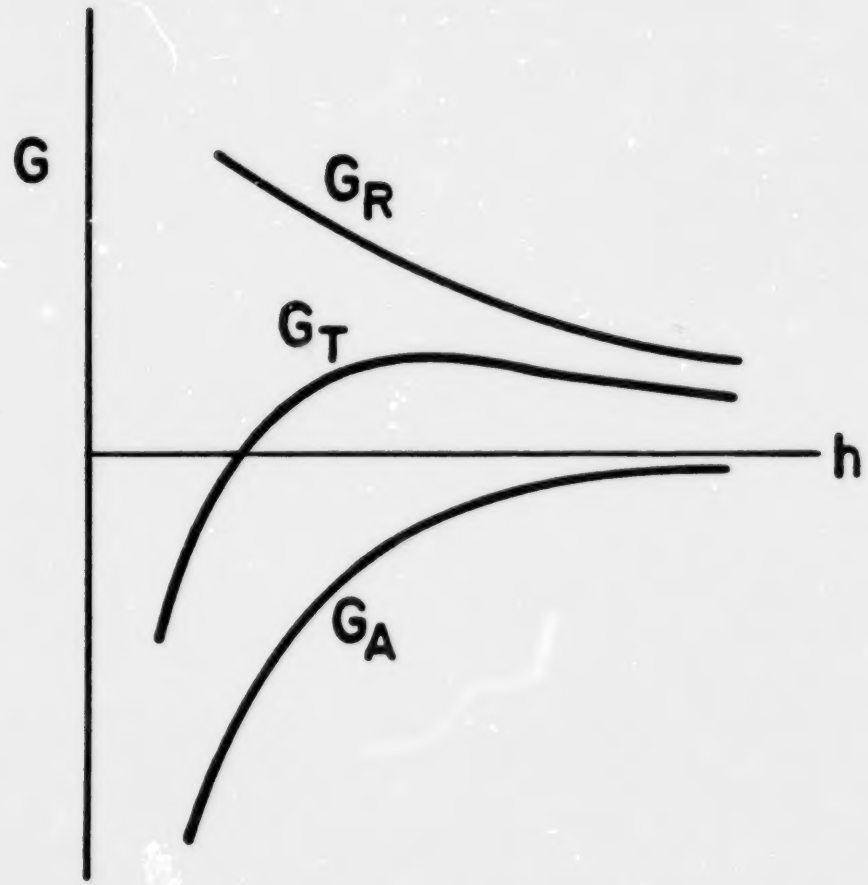

Figure 4 - Potential energy of particles in non-polar media.

energy with regard to separation at an infinite distance. Consequently, the energy barrier is lowered and the stability against flocculation diminished. By taking into account interactions between large numbers of particles, the rapid flocculation of these W/O systems can be explained (Albers and Overbeek, 1959a). In fact, in most non-polar continuous media, G_R can be safely assumed to be zero (Sherman, 1970). As will be discussed later, most oil field emulsions are stabilized against coalescence by highly rigid films formed on the surfaces of droplets (Blair, 1959; Reisberg and Doscher, 1956; Strassner,1968; Jones et al., 1978; Neustadter et al., 1981; Eley et al., 1987; Mukherjee and Kushnick, 1988).

6. Rate of Flocculation:

Flocculation is the process in which the droplets have not entirely lost their identity and the process can be reversible. Kinetically, flocculation is a second order reaction since it depends, in the first instance, on the collision of two droplets and is expressed in the form (Sharma and Shah, 1985)

$$-\frac{dn_1}{dt} = K_1 n_1^2 \qquad (15)$$

where and n_1 is the number of droplets present after time t. The rate constant, K_1, depends on the frequency of the collision between droplets and is governed by the repulsive forces between them.

2.2.C. COALESCENCE

When two droplets come in contact, in a cream or a floc, or as a result of hydrodynamic flow, the behaviour of the system is governed by the interplay of hydrodynamic forces and surface forces. The radial flow of fluid from

between droplets exerts a shearing force on them, tending to generate a circulation within each droplet. The distortion of the droplets is opposed by surface forces (interfacial tension), because any departure from spherical form involves an increase in the free energy.

When two relatively large drops approach each other and when inertial forces are large compared with surface forces, the flow pattern known as dimpling is observed. This is shown is Figure 5A, liquid being temporarily trapped near the line of approach of the drops because of concave depression in their surfaces. In a dimpling system, the thinnest regions of liquid separating the drops are in the ring forming the periphery of the dimple and it is here that collapse and coalescence will occur if the drops are not protected by an emulsifying agent.

When two small droplets approach each other (or when two large droplets approach each other slowly), dimpling does not occur. The faces of the drops are necessarily depressed while the continuous phase is squeezed out from between them, but they remain convex (Figure. 5B). Thus the place of closest approach of the surfaces of the two drops is on the line of centers and in an unprotected system coalescence will occur at this point as soon as intervening liquid has drained away.

When surface active agents are present, the time of coalescence is greatly extended compared to the emulsions without them. In this case, a thin liquid lamellae is forced between the drops, as shown in Figure 5C, which indicates the operation of surface forces opposing the thinning. The surface interactions are regarded as arising from a disjoining pressure acting at right angles to the plane of the liquid and proportional to the thickness of the film. The thin liquid lamellae are inherently unstable. They are subject

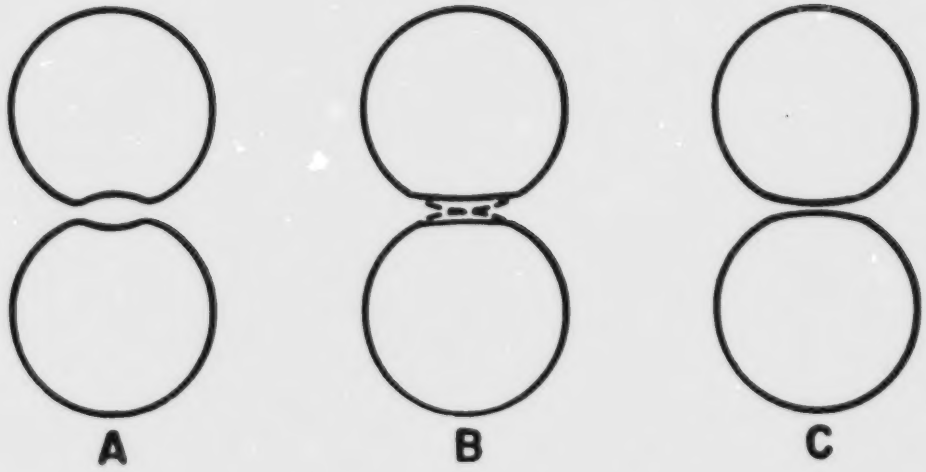

Figure 5 - Approach of two drops.

to a negative disjoining pressure which increases in magnitude as the film thins. In this regard, it has been observed that there exists a critical film thickness for the sudden onset of collapse in the absence of a protective mechanism.

Finally, it has been proposed that percolation enhanced coalescence could also play a role in destabilizing emulsions (Hazzlet and Schechter, 1988; Mukerjee and Kushnick, 1988). That is, when the continuous phase surrounding the dispersed phase contains swollen micelles or is a microemulsion, the thin films separating the drops can rupture at larger distances than predicted by DLVO theory. In this phenomenon, submicroscopic structures which exist as a part of the continuous phase provide large scale pathways for bulk transfer between corresponding droplets. Therefore, film thinning occurs until the film becomes unstable because of the long range van der Waals attraction or because the swollen micellar structures form a continuous percolating network from one droplet to the other.

1. **Rate of Coalescence:**

Coalescence is the secondary process during which the number of droplets decreases leading to a stage of irreversibility and finally complete demulsification takes place. The rate of coalescence is likely to depend primarily on the film-film repulsion, film drainage and the degree of kinetics of desorption (Sharma and Shah, 1985). Kinetically, coalescence is a unimolecular process and the probability of merging of two droplets in an aggregate is assumed not to affect the stability at other point of contact. Therefore, it can be expressed in the following form

$$-\frac{dn_2}{dt} = K_2 n_2 \qquad (16)$$

where n_2 is the number of individual droplets after time t. The rate constant, K_2, depends on the lateral adhesion properties of the surfactant film at the interface

2.3 INTERFACIAL FILMS IN WATER-IN-CRUDE OIL EMULSIONS

The stability of emulsions commonly encountered in crude oil production results from formation of mechanically strong films at the crude oil-water interface. These viscoelastic films act as mechanical barriers to coalescence and hence the emulsion stability is high. That is , the water droplets are sterically stabilized by the asphaltene and resin fractions of the crude oil (King, 1941; Reisberg and Doscher, 1956; Blair, 1959; Kimbler et al., 1966; Strassner, 1968; Uzoigwe and Marsden, 1970; Mackay et al., 1973; Petrov and Blatova, 1974; Neustadter and Whittingham, 1975; Jones et al., 1978; Neustadter et al., 1981; Thompson et al, 1985; Eley et al., 1987; Eley et al, 1988a; Muhkerjee and Kushmick, 1988; Decker and Flock, 1988). These are condensed aromatic rings containing saturated carbon chains and napthenic rings as substituents, along with a distribution of heteroatoms and metals. They are capable of crosslinking at the water drop-oil interface. This primary film may be augmented by secondary adsorption of large particles or micelles originally suspended in the crude oil such as formation fines, crystalline wax and asphaltenes at the point of incipient precipitation (Blair, 1959; Strassner, 1968; Smith and Ramsden, 1978; Thompson et al, 1985; Eley et al., 1988a). The interfacial films formed by different crude oils have markedly different characteristics. The physical characteristics of the films are a function of crude oil type and gas content, composition and pH of water, temperature, presence of non-ionic polar molecules in water, extent to

which the adsorbed film is compressed, contact time allowed for adsorption, and concentration of polar molecules in the oil phase (Kimbler et al., 1966; Jones et al., 1978).

When two water droplets approach each other, the resistance of the oil film being squeezed out has two contributions (Petrov and Blatova, 1973). The first one is the resistance of the oil film which arises as the oil flows out of the film. Hydrodynamic interactions between the interfacial film and inlaying liquid means that drainage of oil from the layer between two approaching water drops creates a local expansion of the interface. The resulting surface tension gradient then creates a force which opposes thinning (Maragoni effect). The second one is the resistance determined by the specific properties of the thin liquid interlayers and the structural-mechanical properties of the interfacial layers of the natural surfactant around the water droplets, i.e., the strength and thickness of the film. The coalescence of these water droplets in a W/O emulsion is accompanied by an initial increase in surface area as the drops form a connecting neck in a dumb bell configuration and subsequent reduction in surface area and hence the compression of the oil-water interface as the drops coalesce. Several phenomena may occur during compression: solvent molecules may be squeezed out of the film, surfactant molecules not tightly held in the interface may redissolve into the bulk phase and molecular rearrangement may occur. In a mixture as complex as crude oil, numerous surface active species occur. The initial compression of the interface causes a continual rejection of weakly adsorbed materials with progressively increasing compression to a point where highly adsorbed species remain at the surface in a closed-packed rigid film. (Reisberg and Doscher, 1956; Blair, 1959; Jones et al., 1978; Neustadter,

1981; Eley et al., 1986).

It has been reported that high temperatures do not prevent the formation of rigid films (Reisberg and Doscher, 1956; Stranner, 1968). However, this may not always be the case. If the increase in temperature corresponds to dissolution of wax particles from the interface to the oil phase, this may destabilize the emulsion in waxy crude oils. On the other hand, for asphaltenic crude oils, an increase in temperature which favours the dissolution of the waxes does not eliminate the stabilizing action of asphaltenes and resins (Petrov and Blatova, 1974; Smith and Ramsden, 1978; Thompson et al. 1985; Stockwell et al., 1986).

During the coalescence of water droplets, the oil in the liquid film between the droplets has to drain out, thereby thinning the film and finally rupturing it. The faster the film thins, the greater the rate of coalescence. The liquid drainage rate depends, among other factors, on the interfacial shear viscosity. A high interfacial viscosity slows down the liquid drainage, consequently the emulsion is stable. But the reverse is not true. That is, emulsions have been found to be stable even with low interfacial viscosity (Neustadter et al., 1975; Jones et al., 1978). In those cases, where the interfacial viscosity is low, high values can be generated by compression of the interface. It has been shown that low interfacial viscosity is a necessary but not a sufficient criterion for emulsion instability. In particular, low dynamic interfacial tension gradients can be correlated with the instability in systems with low interfacial viscosity (Mukherjee and Kushnick, 1988).

Temperature can also lead to significant changes in the interfacial viscosity behaviour. As distinct from the bulk viscosity, which falls with an

increase in temperature, the interfacial viscosity may fall, increase or remain unchanged, depending on the interface. Although the effect of heat on the interfacial film characteristics has not been adequately studied, it has been observed that many incompressible, non-relaxing films start to relax at higher temperatures. However, this observation may also depend on the system pressure. In other words, changes in the solvent properties of the crude oil for the natural surfactants due to loss of light ends at lower pressures will also affect the film compressibility and temperature sensitivity. It has been noted that some crude oils (not all) show a sensitivity to loss of light ends in the form of altered solvency. This may cause significant changes in the interfacial viscosity and compressibility with the age of crude oil. Consequently, a rigid, incompressible, non-relaxing film is formed which remains insensitive to changes in temperature. The changes are more strongly related to release of gas from the crude oil than to actual sample age (Jones et al., 1978)

The presence of ions in the aqueous phase may alter the physical characteristics of interfacial films by a number of mechanisms (Kimbler et al., 1966). First, the ions may react with hydrophilic groups to form insoluble salts. Specific ion effects are also important because formation water that can be associated with oil field emulsions may vary greatly with respect to salt content. For example, with North Sea crudes, incompressible, non-relaxing films, which are temperature sensitive, result where formation waters have a high Ca^{++} to low Mg^{++} ion ratio, irrespective of total salinity (Jones et al., 1978, Neustadter, et al., 1981). Second, salts act to increase the area of a monolayer and lead to a more expanded phase state in the absence of chemical effects. (Hawkins, 1951). This effect is usually associated with

the air-water interface, and the degree to which it applies to an oil-water interface is not clear. Third, ions are negatively adsorbed at a water surface. This effect leads to a layer of pure water, the thickness of which is inversely proportional to the ionic concentration. As a result, electrostatic effects may become more pronounced as the ionic concentration is increased. Finally, where surface films are charged, a charged surface exists below the interface (Donnan effect). A diffuse layer of counterions will exist below this surface and result in an electrostatic contribution to the surface energy.

The pH of the aqueous phase has an important effect on interfacial films as well. The interfacial tension between NaOH solutions and the crude oil have been found to be low (McCaffery, 1976; Fiori, 1983). Furthermore, adjusting pH significantly affects the film-forming, oil wetting and emulsion stabilizing properties of the polar asphaltene and resin fractions. In particular, the rigid interfacial films formed by asphaltenes are strongest in acid pH, intermediate in strength in neutral pH and become very weak or are converted to mobile films in basic pH (Reisberg and Doscher, 1956; Kimbler et al., 1966; Strassner, 1968). The actual pH values at which the film properties change varies widely for crude-brine systems. At high pH values, acidic compounds in the crude oil react with sodium ions at the interface and form sodium soap products which are capable of displacing the interfacially active asphaltic aggregates responsible for the rigidity of the neutral or acidic interface. This also causes the sodium products to subsequently migrate away from the interface causing a rapid rise in the interfacial tension (McCaffery, 1976; Rubin and Radke, 1980; Plegue et al., 1986).

Finally, the rheological properties of the adsorbed emulsifier film has

an important effect on the deformation of droplets. These film properties are of some significance in concentrated dispersions. There are no methods for studying the rheological properties of these films in-situ in the emulsion. The standard procedure is to study films which are developed at a flat, extended interface between bulk water and the oil phase. There is some doubt whether the results of such investigations can be applied to the behaviour of emulsifier films in sheared emulsions, because in the latter the films are far from flat, and the pronounced curvature may exert an important effect (Sherman, 1970).

As has been summarized above, crude oil emulsions are stabilized by viscoelastic highly rigid films. Water droplets in such emulsions behave like rigid spheres (Sherman, 1955, 1968a, 1970; Bechter, 1977; Sherman, 1983). Therefore, theories developed for solid particle dispersion should, in principal, be applicable to oil field emulsions which are mostly of the W/O type.

2.4 RHEOLOGY OF EMULSIONS

The behaviour of an emulsion when sheared, in flocculation, depends upon its composition and the chemical nature of its ingredients. The rheology of emulsions has received far less attention than the rheology of dispersions because emulsions are much more difficult systems to study. In emulsions a deformable fluid constitutes the internal phase, and the emulsifier establishes a third phase in the form of a layer adsorbed around the particles which modifies the cohesion between the particles, and also the forces between the particles and the continuous phase. Consequently, there is a tendency to draw upon the theories developed for solid particle dispersions whenever

possible. However, this may not be a bad assumption, as has been mentioned in the previous section, in the case of water-in-crude oil emulsions stabilized by rigid films.

When interpreting rheological data for emulsions, it should be appreciated that many factors may exert some effect. Although the effect of each factor will be reviewed separately; in practice, two or more factors operate simultaneously and the net effect differs in magnitude from the sum of individual contributions. If the interactions between various factors is ignored, the interpretation of experimental data and the conclusions drawn from it may not be valid (Sherman, 1968a, 1970).

2.4.1 DISPERSED PHASE CONCENTRATION

The viscosity of an infinitely dilute (no particle interactions) suspension of neutrally buoyant, non-deformable spheres in a Newtonian fluid was derived by Einstein in 1906. He assumed that the diameter of the monodisperse spheres was large compared to molecular dimensions but small compared to the characteristic length of the measuring instrument and that there was no slip at the sphere surface. Under these conditions, the viscosity of the suspension μ arises only from the dissipation of energy, or viscous drag, which is produced by modification of the fluid motion in the proximity of the particle surfaces, and is given by

$$\mu_{rel} = \frac{\mu}{\mu_o} = 1+a\phi \qquad (17)$$

where μ_o is the viscosity of the continuous phase, ϕ is the volume concentration of the dispersed particles, and constant a equals to 2.5. Equation (17) is generally valid up to the order of $\phi = 0.01$ (Thomas, 1965;

Sherman, 1968a, 1970). The actual limiting value depends on the particle size, for which no allowance was made in Equation (17).

At low concentrations, the suspensions generally behave like a Newtonian fluid. If a certain value of particle concentration is exceeded, the behaviour becomes non-Newtonian. The transition point depends on the particular system used and can be as high as $\phi = 0.50$ and as low as $\phi = 0.10$ (Sherman 1968a, 1970; Uzoigwe and Marsden, 1970; Jinescu, 1974; Mao and Marsden, 1977; Frankel and Acrivos, 1976; Alvarado and Marsden, 1979; Steinborn and Flock, 1983; Pal and Rhodes, 1984, Stockwell et al., 1986). In general, however, Equation (17) is valid for $\phi < 0.1$; up to a value where the experimental data verify the linear relationship between μ and ϕ. In this region, the constant a can be as large as 5.5 (Thomas, 1965; Jinescu, 1974).

At concentrations higher than a critical value, it is necessary to take into account hydrodynamic interactions between particles, particle rotation, collision between particles, mutual exclusion of particles, double and higher order agglomerate formation, and ultimately the mechanical interference between particles. This causes the viscosity to increase rapidly with concentration. Many of the equations derived by theoretical or experimental means can be usually reduced to a power series in ϕ (Sherman, 1983),

$$\mu_{rel} = 1 + 2.5\,\phi + b\phi^2 + c\,\phi^3 + \ldots \qquad (18)$$

where b and c are constants. The Arrhenius relationship given by

$$\mu_{rel} = \exp(a\phi) \qquad (19)$$

can be expressed in the form of Equation (18) by expanding the exponential function in series.

When the emulsions exhibit non-Newtonian flow, μ_{rel} in Equations (18) and (19) represent the ratio of the limiting viscosity at high shear rates to μ_o. The main drawback is that the termination of series after the ϕ^2 term means a 10% or greater error in the viscosity ratio for $\phi > 0.15 - 0.20$; the inclusion of the ϕ^3 term extends the validity of the series form to $\phi \simeq 0.40$. The values suggested, in the literature, for the constant b range from 0 to 14 and for the constant c from 15 to 16 (Sherman, 1970; Jinescu, 1974; Mewis and Spaull, 1976). The lack of agreement between the values obtained by various investigators for b and c is due to complex interactions, taking place at high concentrations and which are difficult to treat theoretically, as well as to random manifestations of these interactions.

It has been suggested that Equation (18) can be modified by allowing for the probability of a globule being transferred from the plane of shear to another plane at infinitely high shear where aggregation is absent. This may be done by choosing an exponential form for the $c\phi^3$ term in Equation (18) as follows (Thomas, 1965),

$$\mu_{rel} = 1 + 2.5\,\phi + 10.05\,\phi^2 + A \exp(B\phi) \qquad (20)$$

The constants A and B in this equation were obtained by curve fitting the experimental data which has been corrected for scatter by taking into account differences in particle size and shear rates used by various researchers ($A = 0.00273$, $B = 16.6$). This equation gives good results up to a concentration value of 0.60.

The sharp increase in viscosity which is observed in more concentrated emulsions can be explained by applying lubrication theory to calculate the viscous dissipation energy (Frankel and Acrivos, 1967). It was found that

when ϕ/ϕ_{max} approaches one, particle interactions become more ordered due to packing constraints and the viscosity under these conditions is given by

$$\mu_{rel} = \frac{9}{8} \frac{(\phi / \phi_{max})^{1/3}}{1-(\phi/\phi_{max})^{1/3}} \tag{21}$$

where ϕ_{max} is the maximum concentration of dispersed phase which can be incorporated. When particles are in a simple cubic array, $\phi_{max} = \pi/6$ and when they are in a hexagonal closest-packed array, $\phi_{max} = 0.7405$. The value of ϕ_{max} can also be calculated from the experimental data of μ_{rel} as a function of ϕ (Pal and Rhodes, 1984). An equation similar to Equation (21) can be derived by assuming that the thin films of continuous phase between closely packed spherical particles resist the deformation and relative motion of adjacent bounding surfaces and give rise to forces similar to those encountered in hydrodynamic lubrication (Goddart, 1977). For hexagonal packing the same equation as Equation (21) is obtained; but for simple cubical packing the constant 9/8 is replaced by $\pi/8$. Equation (21) was found to be valid for a very limited range of viscosity data, thus its validity has not really been substantiated.

Mooney (1951) proposed an Arrhenius type equation which is given by the following equation

$$\mu_{rel} = \exp \frac{a\,\phi}{1-k\phi} \tag{22}$$

where a is the Einstein coefficient, which is equal to 2.5 when the rigid particles are completely deflocculated, and k is the self-crowding factor.

The factor $1-k\phi$ in the denominator takes into account the dynamic interactions between particles. From purely geometrical considerations it was shown that $1.35 < k < 1.91$ (Mooney, 1951). However, in general k is a function of particle size. An analysis of published experimental data suggests that this relationship can be represented by an empirical relationship of the form (Matsumoto and Sherman, 1969; Parkinson et al., 1970)

$$k = 1.079 + \exp(0.01008/D) + \exp(0.0029/D^2) \tag{23}$$

where D is the particle diameter. Equation (22) can also be expressed in an alternate form as shown below (Gillespie, 1976)

$$\mu_{rel} = \exp \frac{a\phi}{1-(\phi/\phi_{max})} \tag{24}$$

For systems which are not completely flocculated, the constant a can take on values up to 5 (Parkinson et al., 1970; Jeffrey and Acrivos, 1976; Gillespie, 1976). The relationship given by Mooney is in good agreement with experimental data (Jinescu, 1974).

Finally, Eilers' (1941) equation

$$\mu_{rel} = 1 + \left[\frac{1.25}{1-(\phi/\phi_{max})}\right]^2 \tag{25}$$

yields good agreement with the experiments up to a concentration of ϕ_{max}. This equation has the property that when $\phi = \phi_{max}$, the viscosity becomes infinite, i.e. the emulsion ceases to behave as a liquid when the maximum

packing fraction is reached. It has been found for water-in-crude oil emulsions that Newtonian viscosities and extrapolated limiting viscosities for non-Newtonian emulsions can be related to water volume fraction by fitting an Eilers type equation containing two adjustable parameters ϕ_{max} and μ_{int} (Eley et al., 1988b). This equation is a general form of Equation (25) and is given by

$$\mu_{rel} = 1 + \left[\frac{\phi \, \mu_{int}}{2[1-(\phi/\phi_{max})]} \right]^2 \qquad (26)$$

where, in the limit of small ϕ, μ_{rel} becomes linearly dependent on ϕ with a coefficient equal to intrinsic viscosity, μ_{int}.

The general conclusion to be drawn from a survey of published literature is that, at present, there is no single theory which is universally applicable (Jeffrey and Acrivos, 1976; Sherman, 1983). Nevertheless, the viscosity of concentrated emulsions at high shear rates, where drops are completely deflocculated, can often be satisfactorily described by an equation similar to Equation (22) (Sherman, 1983). Furthermore, as a first approximation, Equations (25) (or (26)) and (20) could also be recommended (Jinescu, 1974)).

2.4.2 PARTICLE/DROP SIZE AND SIZE DISTRIBUTION

It is now well understood that the rheology of mono-disperse suspensions containing spherical particles are influenced by the particle size (Richardson, 1950, 1958; Sweeny and Geckler, 1954; Sherman, 1965, 1968a, 1968b, 1970, 1983; Lee et al., 1985; Plegue et al., 1986; Stockwell et al., 1986). In particular, the apparent viscosity increases with a decrease in particle size. This is thought to be a consequence of both an increase in the interfacial area leading to an increase in interfacial viscosity effects

and also an increase in hydrodynamic interactions because of an increase in the number of droplets. The effect of droplet size is more pronounced with higher dispersed phase concentrations (Plegue et al., 1986; Stockwell et al., 1986).

Equations presented in the last section (except for Equation (23)) does not involve any term involving droplet size. Equations proposed for more concentrated emulsions try to take into account the effect of particle interactions by simply incorporating higher powers of ϕ. As viscosity can be changed merely by altering the particle size while maintaining ϕ constant, there is a need to consider explicitly the effect of particle size. Moreover, when observing the effect of the particle size, the state of the emulsion has to be also taken into account (Sherman, 1968a, 1970).

In concentrated emulsions, in order to take into account the effect of particle size (which is no longer insignificant with respect to interdroplet separation and its effect on particle interactions) a concentric spherical enclosure of diameter D_c is drawn around a given reference particle. This enclosure defines the boundary beyond which there is no interaction between the reference particle and the other particles. The value of D_c depends on the dispersed phase concentration and the mean particle size D_m. Thus, Equation (17) can be modified to take into account particle interactions (Simha and Somcynsky, 1965)

$$\mu_{rel} = 1 + aI_H \phi \qquad (27)$$

where

$$I_H = \frac{4\ [1 - (D_m/D_c)^7]}{4\ [1+(D_m/D_c)^{10}] - 25\ ((D_m/D_c)^3\ [1+(D_m/D_c)^4]) + 42\ (D_m/D_c)^5} \quad (28)$$

The factor I_H defines the interaction between the reference particle and all the other particles. It increases slowly until $D_m/D_c = 0.5$; and much more rapidly in the interval $0.5 < D_m/D_c < 1.0$. In dilute systems, D_c is proportional to the distance between particles (h), whereas in concentrated systems it is proportional to $h-D_m$. The value of D_c becomes more significant as the distance between particles decreases with increased concentration.
For dilute systems,

$$\frac{D_m}{D_c} = \frac{\phi^{1/3}}{(8\phi_{max})^{1/3}} \quad (29)$$

and in concentrated systems,

$$\frac{D_m}{D_c} = \frac{\phi^{1/3}}{(8\phi_{max})^{1/3}\ [1 - (8\phi\phi_{max})^{1/3}]} \quad (30)$$

At high shear rates, the particles in a dispersed system are deflocculated, and they are approximately equidistant from one other. If the droplets behave as rigid spheres, the mean distance between them can be calculated from (Sherman, 1963)

$$h_m = D_m\ [(\phi_{max}/\phi)^{1/3} - 1] \quad (31)$$

where the mean globule size can be determined from

$$D_m = \left[\frac{n_1 D_1^3 + n_2 D_2^3 + \ldots\ldots + n_i D_i^3}{n_1 + n_2 + \ldots\ldots + n_2}\right]^{1/3} \qquad 32)$$

where n_1, n_2,...., n_i are the numbers of globules with diameters D_1, D_2,...., D_i, respectively. When μ_{rel} was plotted versus D_m for all the W/O emulsions prepared using a single emulsifier, a single exponential curve was obtained which covered all the values of ϕ (Sherman, 1969).

The mean distance between particles is related to distance L_m over which globules of finite size, on opposite sides of a spherical enclosure, interact in the presence of an influencing globule by (Simha, 1952)

$$L_m = h_m + \frac{D_m}{2} \qquad (33)$$

and the hydrodynamic coefficient I_H can be defined in an alternate way to Equation (28).

$$I_H = \frac{1 - \frac{D_m}{2L_m}}{\frac{D_m}{2L_m}} \qquad (34)$$

For W/O emulsions, a suitable relationship between μ_{rel} vs h_m can be derived when D_m is greater than 1 micron (Sherman, 1965)

$$\ln \mu_{rel} = \ln \frac{\mu_\infty}{\mu_o} = \frac{0.036\ D_m^2}{h_m} - 0.015 \qquad (35)$$

where μ_∞ is the viscosity of the emulsion at high enough shear rate so that it is completely deflocculated. This equation is not valid for polydisperse systems because its form varies with the degree of inhomogeneity of the system.

The relationship given by Equation (27) seems to be unsatisfactory because it does not make any allowance for particle size on viscosity, and consequently, it cannot be valid when particle sizes are below a few microns (Thomas, 1965; Sherman, 1968a, 1970). The dependence of h_m on both ϕ and D_m helps to explain some of the conflicting results in the literature. When D_m exceeds 10-20 microns, it will exert a significant effect on μ_{rel} only at medium to high ϕ (See Equations (31) and (35)). Alternatively, when $D_m < 1$ micron, this effect is apparent at $\phi = 0.05$. The increasing effect of particle size on μ_{rel} for smaller droplets, particularly below 1-2 microns, makes the rheology of these types of emulsions very complex.

All practical emulsions show some form of size distribution and D_m represents the mean value of this size distribution. Model dispersions containing spheres of two different sizes exhibit a minimum viscosity at a certain diameter ratio. However, when more than two sizes of spheres are mixed at a constant total ϕ, no minimum is observed and the viscosity increases curvilinearly as the proportion of the smallest sphere size increases (Parkinson, et al., 1970). In a polydisperse system, the viscosity is smaller than would be indicated by μ_{rel} vs D_m relationship (Richardson, 1958).

In a bimodal suspension, the finer particles behave essentially as a fluid towards coarser particles (Farris, 1968). If the size ratio is less than 0.1, the large spheres encounter the same resistance to motion when

passing through a suspension of smaller spheres as when it passes through a pure liquid of the same viscosity and density. When the size ratio becomes greater than 0.1, the resistance is the same but the particle follows a zig-zag random path instead of a straight line path. This model can be expanded to emulsions containing an i-modal size distribution, so that (Mooney, 1951; Farris, 1968; Parkinson et al., 1970; Sherman, 1983)

$$\mu_{rel} = \mu_{rel(1)}\, \mu_{rel(2)} \cdots\cdots \mu_{rel(i)} \tag{36}$$

where $\mu_{rel(1)}$, $\mu_{rel(2)}$,....., $\mu_{rel(i)}$ are the relative viscosities of different size fractions at the same shear rate for the same concentration that they occupy in the emulsion when they are independently dispersed in the continuous phase. As long as the particles do not exhibit permanent flocculation, Equation (36) can be modified to a Mooney type equation by using Equation (22),

$$\mu_{rel} = \exp \frac{2.5\phi_1}{1-k_1\phi_1} \exp \frac{2.5\phi_2}{1-k_2\phi_2} \ldots\ldots \exp \frac{2.5\phi_i}{1-k_i\phi_i} \tag{37}$$

where constants k_1, k_2,....., k_i associated with each different diameter can be calculated from Equation (23). A comparison of experimental μ_{rel} data for both O/W and W/O emulsions with values calculated from Equation (37) shows good agreement. The agreement extends to higher values of ϕ for the W/O emulsions (up to $\phi = 0.6$) than for the O/W emulsions (up to $\phi = 0.4$) (Parkinson et al., 1970). The discrepancy arising for the very concentrated O/W emulsions may be due to the drops being larger than in W/O emulsions, and therefore, the possibility of drop deformation being greater (Sherman, 1983).

Many factors influence the viscosity of an emulsion. It is possible that

some of these factors act, at least, partly by altering the particle size distribution. Consequently, if other effects are to be identified quantitatively, it is necessary to know how the particle size and/or particle size distribution affects viscosity. Similarly, when comparing viscosity data for emulsions with the same D_m, it is necessary to determine whether the size distribution patterns are the same. In the absence of such knowledge, incorrect conclusions may be drawn.

2.4.3 VISCOSITY OF DISPERSED PHASE (PARTICLE DEFORMATION)

A drop of liquid in motion through another liquid differs in behaviour from a solid sphere in that it may be deformed or have a circulation set up within itself by the shearing effect of the relative motion of the two fluids. These effects upset the stability of the drop, causing it to oscillate about the spherical shape and eventually burst into fragments or, at least, into smaller droplets. Before bursting, the effects of deformation and circulation become apparent as a decrease in the resistance, compared to that of a rigid sphere of the same diameter. Some irreversible work is done in distorting the globules. Consequently, droplet deformation and internal circulation leads to negative deviations from viscosities calculated from previous equations.

Einstein's equation has been extended to dilute suspensions of fluid particles (Taylor, 1932). The normal or tangential stresses are transferred from the continuous phase to the dispersed phase assuming that there is no slippage at the interface and that the emulsifier film around particles does not hinder the transmission. Under these circumstances, stresses transferred cause fluid circulation within the globules, and this reduces the distortion of the flow patterns around the particles. The precise effect depends on the

ratio μ_i/μ_o as given by

$$\mu_{rel} = 1 + a\left[\frac{\mu_i + (2/5)\,\mu_o}{\mu_i + \mu_o}\right]\phi \qquad (38)$$

where μ_i is the dispersed phase viscosity and the term is square brackets accounts for the internal currents within droplets. When $\mu_i >> \mu_o$, Equation (38) reduces to Equation (17), but under all other conditions μ_{rel} is lower than that for a dispersion of solid particles with the same volume concentration. This equation was extended into a power series in ϕ so as to extend its range of validity to $\phi \simeq 0.40$ as follows (Leviton and Leighton, 1936)

$$\ln \mu_{rel} = a\left[\frac{\mu_i + (2/5)\,\mu_o}{\mu_i + \mu_o}\right](\phi + \phi^{5/3} + \phi^{11/3}) \qquad (39)$$

It should be noted that this equation degenerates to Equation (38) for low volume concentrations. Internal circulation is always reduced to some degree when surface active materials are adsorbed around the globules. Liquid flow around the globules causes adsorbed material at the front to be swept to the rear, and this produces a surface pressure gradient. A gradient of a few dynes/cm^2 is sufficient to prevent motion within the globules, so that they act as drops of liquid of high viscosity, or even as solid spheres (Sherman, 1968a).

In many emulsions, such as oilfield emulsions, the droplets are surrounded by a viscoelastic emulsifier film. If this film withstands the increase in equilibrium interfacial tension with an increase in the surface area, the globules behave as rigid spheres, and the ratio μ_i/μ_o does not influence the emulsion viscosity. However, if the emulsifier film is viscous

the values of parameters may be altered even through the rheological behaviour of the emulsion is not influenced. In this case, the viscosity is given by (Oldroy, 1953, 1955),

$$\mu_{rel} = 1 + a\left[\frac{\mu_i + 2/5\ \mu_o + 2/5\ (2\mu_S + 3\mu_B)\ (2/D)}{\mu_i + \mu_o + 2/5\ (2\mu_S + 3\mu_B)\ (2/D)}\right]\phi \qquad (40)$$

where μ_s and μ_B are the shear viscosity and area viscosity, respectively, of the emulsifier film. The viscous interfacial film has an effect which is equivalent to increasing μ_i by (2/5) $(2\mu_s + 2\mu_B)$ (2/D).

Relative deformation, D^*, of spheres due to hydrodynamic forces in steady shear of dilute emulsions has been shown to be given by (Taylor, 1934; Goldsmith and Mason,, 1967),

$$D^* = \frac{\pi D\mu_o\gamma}{\sigma}\left[\frac{1 + (19/16)\ (\mu_i/\mu_o)}{1 + (\mu_i/\mu_o)}\right] \qquad (41)$$

where σ is interfacial tension and γ is the shear rate. It has been shown that for heavy oil-in-water emulsions ($\mu_i/\mu_o \simeq 100{,}000$) even at a high shear rate of 1000 sec^{-1}, the predicted deformation is small as Equation (41) gives D^* values on the order of 10^{-3} (Plegue et al, 1986). A theoretical equation, which gives the viscosity of moderately concentrated dispersions and which takes into account droplet deformation due to particle interactions as well as hydrodynamic effects, predicts reduced viscosity due to droplet deformation (Choi and Schowalter, 1975). However, at high μ_i/μ_o ratios (on the order of 10^5) this equation reduces to the rigid sphere case.

Furthermore, it has been already mentioned that water-in-heavy oil emulsions encountered in oil fields are stabilized by highly rigid, non-relaxing interfacial films. Therefore, it can be concluded that emulsions

found in heavy oil fields should have negligible particle deformation.

2.4.4 CONTINUOUS PHASE

Virtually all theoretical or empirical treatments of emulsion viscosity consider the viscosity of the continuous phase to be of prime importance in defining the viscosity of the final emulsion as has been seen in the previous sections. All the equations indicate a direct proportionality between viscosity of the emulsion and that of the continuous phase. Most of the published equations may be put in the form (Bechter, 1977),

$$\mu = \mu_o\ (x) \tag{42}$$

where x represents the summation of all other properties which may influence the viscosity. It should be noted that μ_o is the viscosity of the entire continuous phase, and not merely the viscosity of the basic fluid to which the emulsifiers, hydrocolloids, finely-divided solids, etc. are added. If the continuous phase behaves like a non-Newtonian fluid as a result of these additions, the emulsion will also show non-Newtonian behaviour even when it is very dilute (Sherman, 1968a).

In dispersed systems μ_o is slightly, but usually insignificantly, reduced by the adsorption of emulsifier at the globule surfaces. Thus, in most cases, μ_o can be safely assumed to correspond to the viscosity of the continuous phase in bulk. However, this assumption may be incorrect in the light of the fact that the viscosity of a thin film of liquid (emulsifier) is very much higher than the viscosity of the same liquid in the bulk (Sherman, 1970). This is true for both polar and non-polar films. That is, in concentrated dispersed systems in which particles are separated by very thin films of

continuous phase, it is possible that the viscosity of bulk continuous phase is no longer representative of the value of μ_o. Consequently, these type of emulsions may exhibit very high viscosities due to an abnormally high μ_o value. Conversely, the initial rapid decrease in viscosity when shear is applied to a flocculated emulsion may be due in part to a decrease in μ_o as the distance between globules increases with partial or complete deflocculation (Sherman, 1968b, 1970).

2.4.5 SURFACE ACTIVE AGENTS

Having described the various complex rheological characteristics of emulsions, an attempt can be made to show some of the expected effects that may be produced by surfactants which are present in the emulsion. Part of the influence exerted by the surfactant on viscosity may arise from simple geometrical effect. That is, adsorbed surfactant layers cause an increase in hydrodynamic volume of the dispersed droplets (Sherman 1968a, 1970; Tadros, 1984).

While the explanation of increased dimensions of droplets with increased adsorption of the emulsifier may be true in certain instances, it is highly probable that many emulsifiers form films with a thickness of one molecule (Sherman, 1968, 1970). When a condensed monomolecular layer has been established, there is no further adsorption on the particle surface, and any excess emulsifier molecules remain in the continuous phase where they associate to form micelles. These micelles immobilize continuous phase liquid within themselves. Immobilization of continuous phase alters the volume ratio of the dispersed phase to "free" continuous phase, thereby causing an increase in viscosity (Sherman 1968a, 1970; Bechter and Schick, 1987). The degree of

fluid immobilization increases as the excess of emulsifier increases. Finally it has been shown that the value of ϕ at which a Newtonian emulsion becomes non-Newtonian depends on the emulsifier concentration as well (Alvarado and Marsden, 1979). This may be again a result of increased micelle formation in the continuous phase.

Hydration of the surfactant layer adsorbed around droplets in an emulsion will also influence the rheological properties. The viscosities of O/W emulsions stabilized with sodium naphtha sulphonates increase as the emulsifier concentration is increased at any constant value of ϕ. This effect is attributed to an electroviscous effect arising from ionization of the adsorbed sulfonate molecules which creates an electrical double layer. (Sherman, 1983). Furthermore, in general with all ionic surfactants, these systems are expected to show viscoelastic behaviour at low electrolyte concentrations, which in view of the long range of the interaction may be manifest at low ϕ values, particulary with small particles (Tadros, 1984).

2.5 RHEOLOGY OF FLOCCULATED EMULSIONS

Following formation, the drops in emulsions flocculate forming doublets, triplets and higher numbered structures in the absence of shear. The size of aggregates so formed increases with time. When droplets flocculate in an emulsion, part of the continuous phase is immobilized within the aggregates. Thus, a synergistic effect is present, i.e. each aggregate behaves as if the volume is greater than the sum of volumes of individual droplets.

At very low shear rates, elastic behaviour is to be expected (Michaels and Bolger, 1962; Sherman, 1967b, 1968b; Mewis and Spaull, 1976). That is, the flocs group into clusters, or aggregates which may form networks extending

to the walls of the container and giving the emulsion a finite yield stress.

At low shear rates, the aggregates are deformed and reduced in size as shear rate increases. The extent of agglomeration is a function of the shear rate of the measurement and the balance of attractive and repulsive forces (Plegue et al., 1986). The aggregates rotate around their centres of masses like single particles. When these emulsions are examined in a viscometer at low shear rates such that the aggregate structure is not seriously damaged, an anomalously high viscosity is exhibited. At higher rates, the aggregate size is progressively reduced and the volume of continuous phase trapped inside the aggregates are mobilized. Consequently, the viscosity gradually decreases with increasing shear rate (Michaels and Bolger, 1962; Sherman, 1963, 1967a, 1967b, 1968a, 1968b, 1983; Uzoigwe and Marsden, 1970; Mewis and Spaul, 1976; Tadros, 1980, 1984; Steinborn and Flock, 1983; King, 1985). At these high shear rates, although there is no structural network, the flocs may still attract each other in the presence of strong attractive forces. Therefore, shear forces pull floc clusters apart as soon as they form. As a result, there are temporary doublets, triplets, etc. which results from particle-particle collisions. These transient structural effects produce hysteresis loops in the shear stress versus shear rate curves (Michaels and Bolger, 1962). However, if the system is in complete equilibrium in steady state, no hysteresis will be observed in the data (Dreher et al., 1976).

In the flocculated state, an emulsion exhibits viscosity comparable to that of a completely deflocculated emulsion with a higher droplet concentration. This higher droplet concentration, ϕ_a, is defined by (Mooney, 1946; Sherman, 1983)

$$\phi_a = \frac{\pi D^3}{6} N_1 + f (N_t - N_1) \qquad (43)$$

where f is a swelling factor related to the volume of continuous phase immobilized within the drop aggregates, N_t is the total number of drops per unit volume of emulsion at anytime t after formation, and N_1 is the number of unassociated drops per unit volume of emulsion. When flocculation proceeds rapidly with respect to the rate of coalescence, $N_1 \ll N_t$ and $f = \phi_a/\phi$. However, the determination of ϕ_a is a problem. It could be empirically obtained from the following relationship between μ_{rel} and. ϕ (Mooney, 1946; Sherman, 1968a, 1983)

$$\mu_{rel} = \frac{\mu_\infty}{\mu_o} = \frac{1 + 0.5\,\phi}{1 - \phi} \exp \frac{1.25\,\phi}{1 - \phi} \qquad (44)$$

by determining the value of ϕ (ϕ_a) which gives the same μ_{rel} value as the emulsion exhibits at low shear rate with $\mu_{rel} = \mu/\mu_o$. In Equation (44), μ_∞ is the viscosity of the emulsion at infinitely high shear rate so that the emulsion is completely deflocculated. A flocculated emulsion exhibits pseudoplastic behaviour (Albers and Overbeek, 1960; Tadros, 1980, 1984; Eley et al., 1988b). This is shown in Figure 6. The behaviour of such coagulated systems is characterized by three parameters: (i) the critical shear rate,

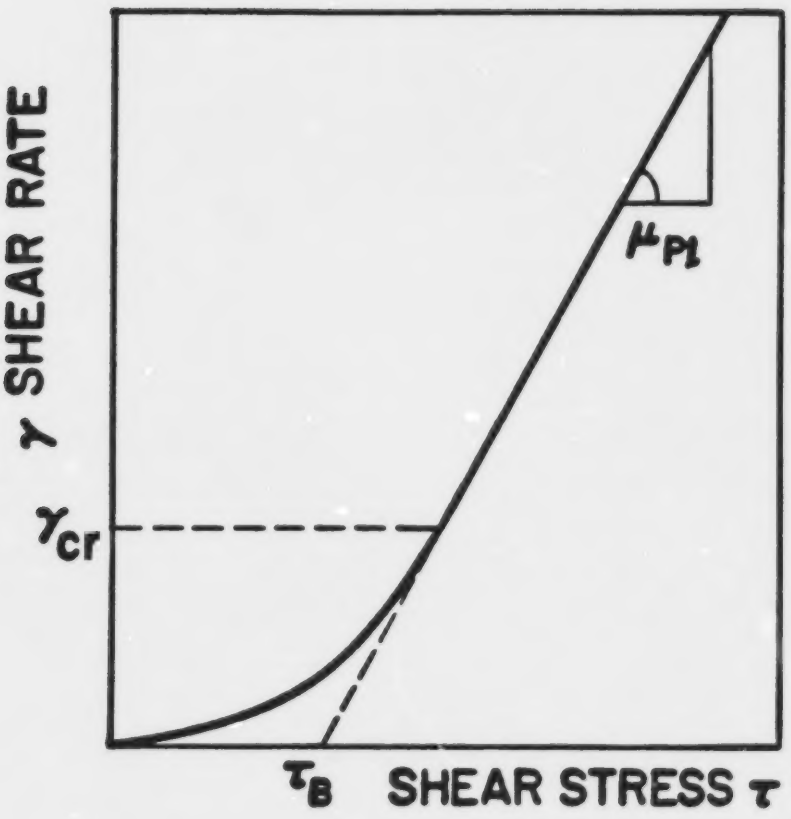

Figure 6 - Flow behaviour of flocculated emulsions.

γ_{cr}, above which the relationship between γ and τ becomes linear, (ii) the plastic viscosity, μ_{pl}, which is the gradient of the linear shear stress-shear rate curve, (iii) the Bingham yield value, τ_B, which is the value of the stress obtained by extrapolating the linear portion of the curve to $\gamma = 0$.

The breaking down of aggregates initially involve the weakest attraction forces between droplets, while the final stage in deflocculation involves the strongest attraction forces. The globules separate when van der Waals attraction is exceeded by the opposing hydrodynamic flow tension which tends to force the globules apart. The critical shear rate, γ_{cr}, at which γ vs. τ curve becomes linear is then the point at which the force of attraction holding the residual pairs of droplets resulting from aggregate breakdown is just exceeded. This value can be calculated from the following equation provided that the emulsion is reasonably mono-disperse and the globules are not deformed (Albert and Overbeek, 1960)

$$\gamma_{cr} = \frac{A}{18\pi \mu_o D_m H^2 S_{in} (2\alpha)} \tag{45}$$

where H is the distance separating globules in the residual aggregate, and α ($\simeq 30^o$) is the critical angle between the line joining the centres of the two globules and the direction of shear at the time when the aggregate undergoes disruption. It has been shown that Equation (43) together with experimental data could be used to estimate the value of Hamaker's constant A (Sherman, 1963) and the thickness of the stabilizing asphaltene film in water-in-crude oil emulsions (Eley et al., 1988b).

Much of the flow behaviour of flocculated colloidal suspensions can be explained with the so called "elastic-floc model" (Frith and Hunter, 1976a,

1976b, 1977). The basic flow unit in such a model is considered to be an elastic floc which will undergo extension and compression during rotation in shear flow and during mutual collision. This model can be used to predict all of the observed dependence of flow parameters on colloidal properties, using reasonable values of the microscopic parameters such as particle approach distance and the number of particle chains involved in floc formation. It was shown that the most important contributions to the energy dissipation are: (a) a viscous energy dissipation due to the presence of spherical flocs in suspension; and (b) the energy dissipated during rupture of floc doublets. Many observable quantities such as μ_{pl}, γ_{cr} and the floc density could be explained satisfactorily using a simple version of the DLVO theory for the interaction forces between particles within a floc.

Both ionic and nonionic surfactants will influence the rheology of unstable suspensions (Tadros, 1984). If the emulsion is weakly flocculated, which may be produced by control of the adsorbed layer thickness, it will behave as a pseudoplastic fluid with a measurable yield value and the appearance of hysteresis in the flow curves. If the emulsion is strongly flocculated, in which strong attraction between the particles dominates the interaction, it will behave as a pseudoplastic fluid with a pronounced yield value.

Finally, when dealing with heavy oil emulsions, the change in viscosity with shear rate may be affected by the formation of multiple emulsions in addition to the breaking up of aggregates (Steinborn, 1982; Steinborn and Flock, 1983). In general, the literature reports the investigation of single phase emulsions and it should be noted that the multiple emulsions may exhibit quite different properties.

2.6 REMARKS ON INVESTIGATIVE APPROACHES

There are two ways to approach the analysis of oil field emulsions (Napper and Hunter, 1977). The first approach is the so called micro-rheological approach which attempts to establish the detailed behaviour of individual particles of various shapes in response to hydrodynamic forces (Goldsmith and Mason, 1967). The second approach is the macro-rheological approach which uses a variety of procedures, some drawn from the micro-approach. The macro-rheological approach establishes a theoretical relationship between the viscosity or the shear stress and the shear rate.

In each category there are mathematical analyses which seek to represent the time evolution of the stress-strain tensor in terms of the properties of the materials. In addition, there are empirical correlations between a parameter related to applied stress and another related to rate of strain or strain itself. In general, the application of physico-chemical methods of analysis lies somewhere between these two extremes. This is because there is a lot to be gained from the development of a description of macroscopic flow behaviour in terms of the microscopic processes which occur in the flowing systems.

Although studies of idealized suspensions are useful to obtain new forms of constitutive equations, and thus provide a means by which different phenomena are isolated, such derivations often demand severe idealizations. However, engineering problems concerning complex crude oil-brine systems are beyond the validity of idealized approaches. In each of the areas of petroleum engineering (during production, for enhanced oil recovery, acidizing, pipeline transportation) the rheological behaviour of the emulsions must be known. Therefore, phenomenological models, based on macro-rheology,

appear to be the most advantageous method of analysis for emulsions encountered in oil field operations.

3. RHEOMETER FOR HIGH PRESSURES AND TEMPERATURES

Several commercially available instruments can be used for investigating the rheology of water-in-oil emulsions at elevated temperatures and pressures, e.g. Haake Rotovisco D100/300, EG&G Chandler Engineering's RheoChan 7400, and Contraves Rheomat 30 with DC 50 measuring head. None of these appear to be clearly superior in all respects and all are very expensive instruments. Therefore the choice of instrument used is often dictated by economic factors and familiarity of the people involved with a particular instrument. In this project a Contaves Rheomat 30 (RM30) was used with DC 50 measuring head. This instrument was made available (free of cost) to the project by a member company of the Petroleum Recovery Institute.

The Rheomat 30 - DC50 is a rotational viscometer of the concentric cylinder design. End effects are eliminated through the use of conical sections, as is shown in Figure 7. Referring to Figure 7, it can be seen that the measuring cylinder rests inside the rheometer cavity and is free moving. Strong permanent magnets are sealed into the measuring cylinder and the drive shaft which rests above the rheometer lid. Thus, movement in the drive shaft is magnetically coupled to movement in the measuring cylinder itself. During operation, a rotational speed is selected and the drive shaft rotates at that speed. The torque required to rotate the magnetically coupled measuring cylinder at any given speed is directly related to the viscosity of the fluid filling the gap between the rotating and stationary cylinders.

The apparatus required some modifications to its basic design in order to accommodate high pressures and temperatures. Seals and sealing schemes in the

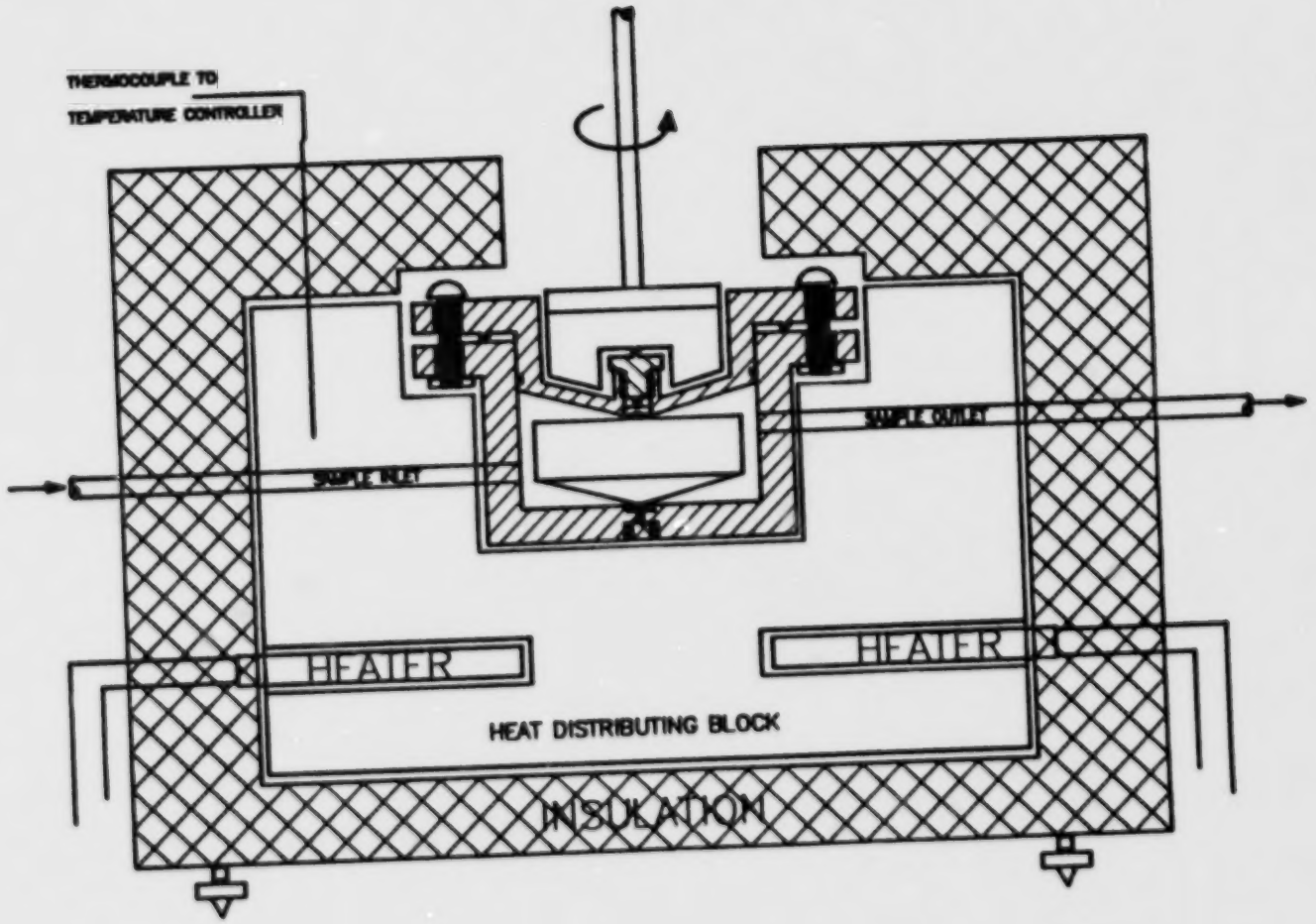

Figure 7: High Pressure Autoclave for Rheomat 30.

main rheometer cavity had to be replaced or redesigned. A special aluminum heating block assembly was created to provide rapid and even heating to the apparatus. The assembly was fitted with leveling devices and a P-I-D temperature controller. Since the emulsions were quite viscous at room temperature, a piston displacement pump was designed and built to pump the emulsions into the rheometer. Also, several pieces of support equipment were built for the rheometer and its parts. These included items such as clamps, cleaning vessels and special tools. Figure 8 shows the current version of the complete assembly. Currently, the device is capable of operating at 4 MPa and 200°C. Following the modifications mentioned above, the completed system was calibrated and tested with several oil viscosity standards that spanned the viscosity range of 1000 to 30000 mPa.s. With the current rotating cylinder and autoclave the viscometer is limited to a viscosity range of 1000 mPa.s to 100,000 mPa.s. We plan to expand this range by acquiring a new measuring autoclave and a new rotating cylinder.

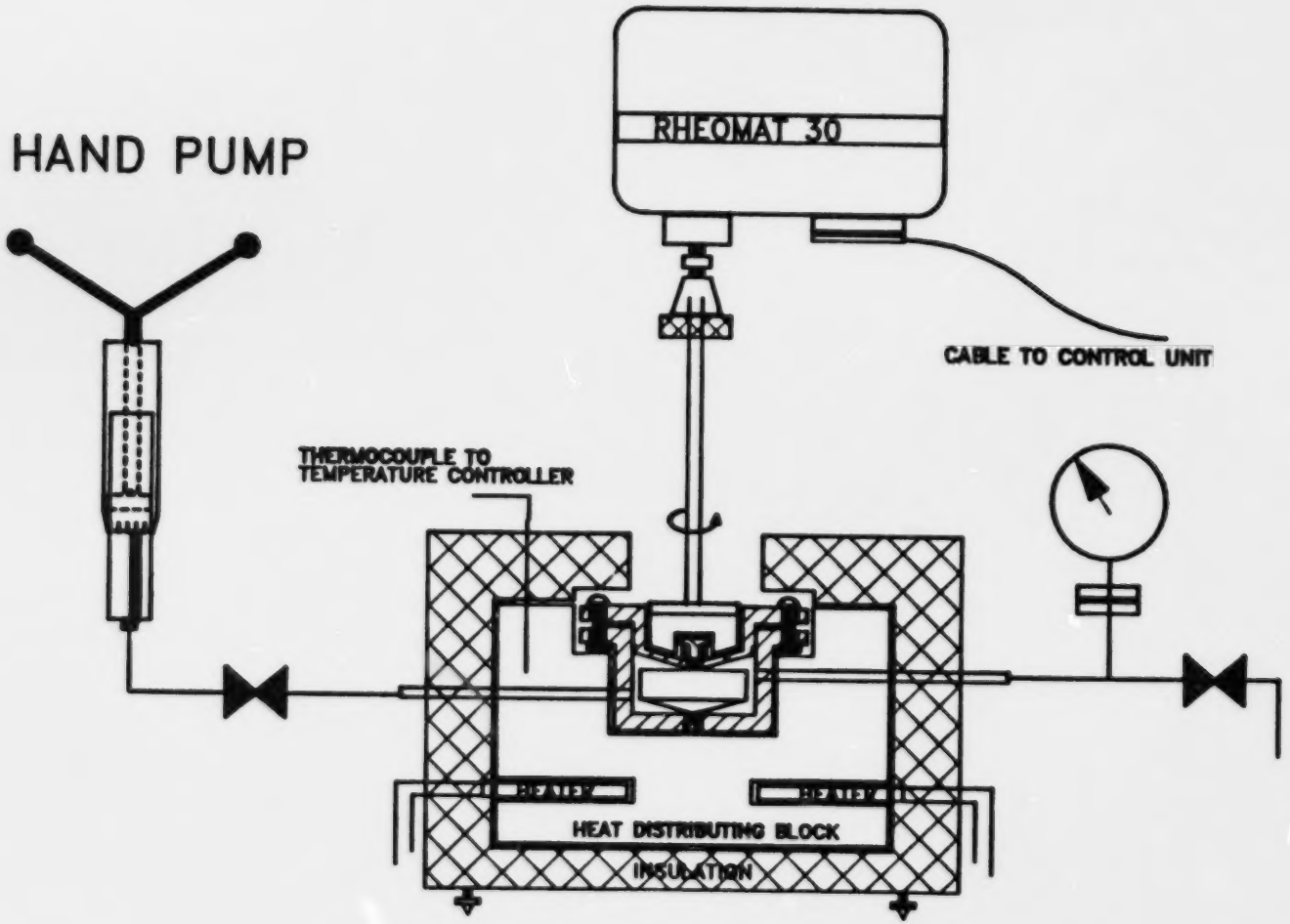

FIGURE 8: MODIFIED RHEOMAT–30 VISCOMETER UNIT

4. RESULTS

4.1 CHARACTERIZATION OF WATER-IN-OIL EMULSIONS

Well head samples of heavy oil were obtained from five different oil reservoirs. One of these was found to be unsuitable for rheology measurements due to its low viscosity (870 mPa.s), which was less than the lower limit of our equipment. When the new measuring autoclave becomes available we will be able to provide such measurements. Four different emulsions were investigated in detail. The first step was to determine the basic characteristics of these emulsions. This included characterization of the oil involved, chemical analysis of the emulsified brine and microscopic examination of the emulsion. Results of these tests are described in the following:

4.1.1 Oil Characteristics.

The properties of the pure oils were measured after removing the emulsified water. This was achieved either by ultra centrifugation or by dilution with methylene chloride to break the emulsion followed by filtration and solvent removal by vacuum distillation. Table 1 compares the densities, viscosities and total acid numbers of the four oils. The distillation characteristics were measured by a simulated distillation technique. These are presented in table 2. The temperature versus viscosity relationship for these oils is shown in Figure 9. Except for the Athabasca sample, the other oils were similar in their viscosity characteristics.

Table 1: Comparison of Oil Properties

Oil	Density At 23.4 °C (g/ml)	Viscosity At 23°C (mPa.s)	Total Acid Number
Athabasca (PCEJ)	1.0104	85,000	1.94
Westmin Lindbergh	0.9798	12,000	0.85
PanCanadian Lindbergh	0.9838	10,000	1.02
Texaco Frog Lake	0.9844	11,000	0.74

Table 2: Comparison of Simulated Distillation Characteristics

	Percent distilled in the boiling range (°C)								
Oil	50-100	100-150	150-200	200-250	250-300	300-350	350-400	400-450	450-525
Athabasca (PCEJ)	0	0	0.8	2.3	4.5	6.1	6.8	7.0	3.4
Westmin Lindbergh	0	0.9	1.9	3.9	5.5	6.0	6.0	5.9	2.9
PanCanadian Lindbergh	0	1.4	1.8	3.9	5.6	6.2	6.2	6.3	3.6
Texaco Frog Lake	0	0	1.2	3.7	6.5	7.4	7.5	7.4	4.4

4.1.2 Brine Characteristics:

The water separated from the emulsions by ultra-centrifugation was analyzed for pH, total dissolved solids and the concentration of various ions. These results are summarized in table 3.

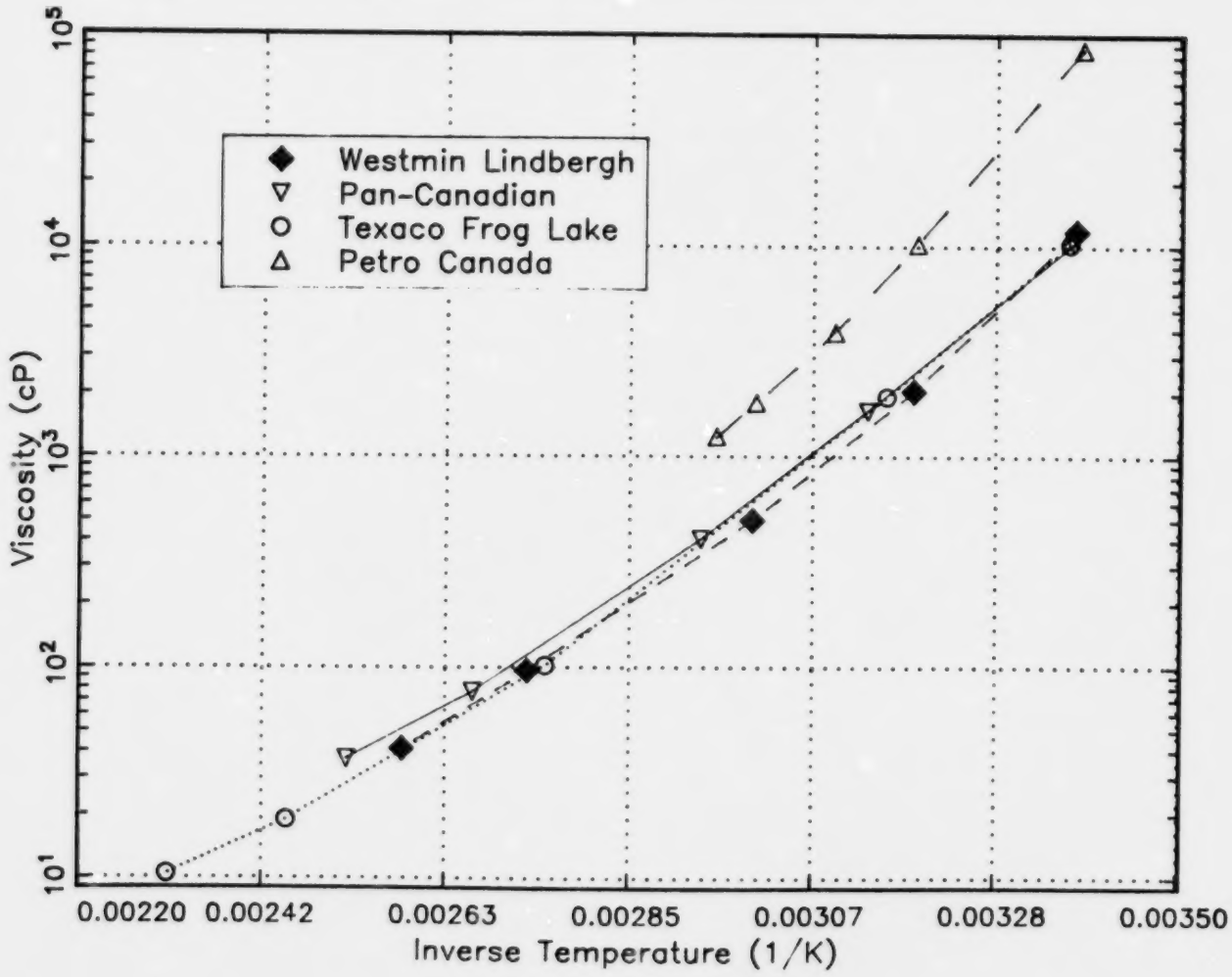
PURE OIL VISCOSITIES
Westmin Lindbergh
Pan-Canadian
Texaco Frog Lake
Petro Canada
Viscosity (cP)
10^1
10^2
10^3
10^4
10^5
0.00220
0.00242
0.00263
0.00285
0.00307
0.00328
0.00350
Inverse Temperature (1/K)

FIGURE 9

Table 3: Brine Analysis

Property	PCEJ Athabasca	Westmin Lindbergh	PanCanadian Lindbergh	Texaco Frog Lake
pH (at 25°C)	8.87	7.4	6.77	6.82
TDS (ppm)	2960	27491	68920	76370
CATIONS: (g/m^3)				
Na	868	9200	23100	24200
K	29.8	53.2	113	180
Ca	3.42	711	1620	1860
Mg	<0.01	332	775	958
Ba	0.07	17.5	48.6	60.2
Sr	<0.01	71.8	168	163
Fe	0.21	0.3	8.4	3.5
B	19.9	3.45	9.11	7.17
ANIONS: (g/m^3)				
Cl	950	16900	41400	45200
HCO3	525	117	123	52.8
CO3	51.9	0.00	0.00	0.00
OH	0.00	0.00	0.00	0.00
SO4	162	84.9	26.4	35.4

4.1.3 Emulsion Characterization:

The amount of water present in the emulsions was determined by the Karl Fischer titration technique. The emulsions were also examined under an

optical microscope to determine the sizes of droplets involved. As shown in table 4, the water content varied from 2.89 weight percent in the Texaco Frog Lake sample to 31.53 weight percent in the PanCanadian Lindbergh Sample.

Table 4: Emulsified Water in Well Head Samples.

Emulsion	Weight Percent Water
PCEJ Athabasca	25.24
Westmin Lindbergh	7.29
PanCanadian Lindbergh	31.53
Texaco Frog Lake	2.89

Figure 10 to 13 show the micrographs of the emulsions. The size of emulsified water drops in the Athabasca sample predominantly ranged from less than 1 $\mu\nu$ to about 5 μm with a few large drops in the 10 to 25 μm range. Unfortunately, we were not able to determine the size distribution precisely due to delays in developing the image analysis software. It is expected that we will have a functional image analysis system in the near future. These micrographs will then be analyzed to define the droplet size distribution. As shown in Figure 11 the Westmin sample had drops ranging from 1 μm to 10 μm. The PanCanadian sample had a much wider size distribution ranging from sub-micron sizes to 25 μm. The size distribution of the Frog Lake sample appeared to be similar to that in the Westmin Lindbergh sample.

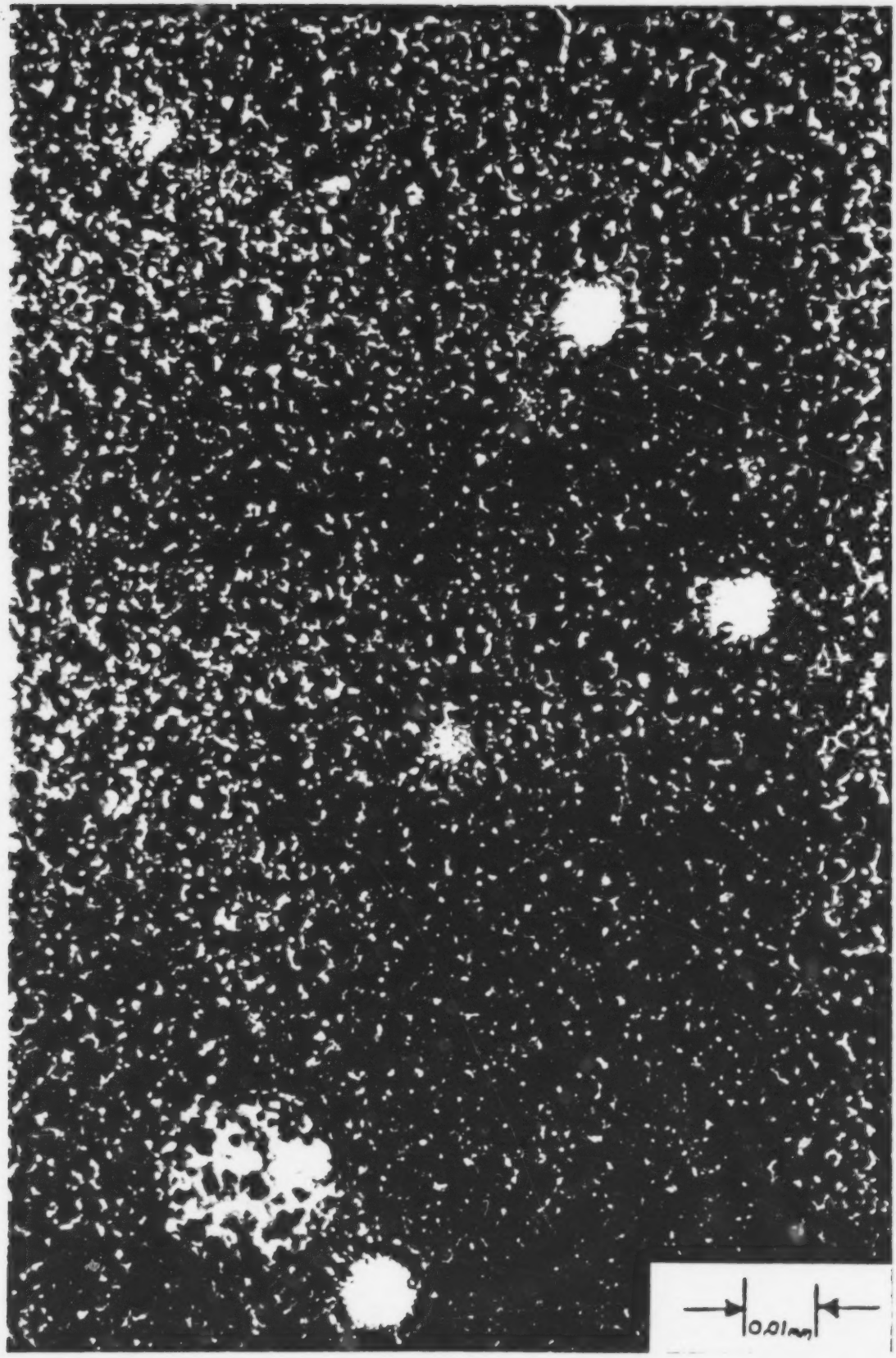

Figure 10: Micrograph of the Athabasca Emulsion

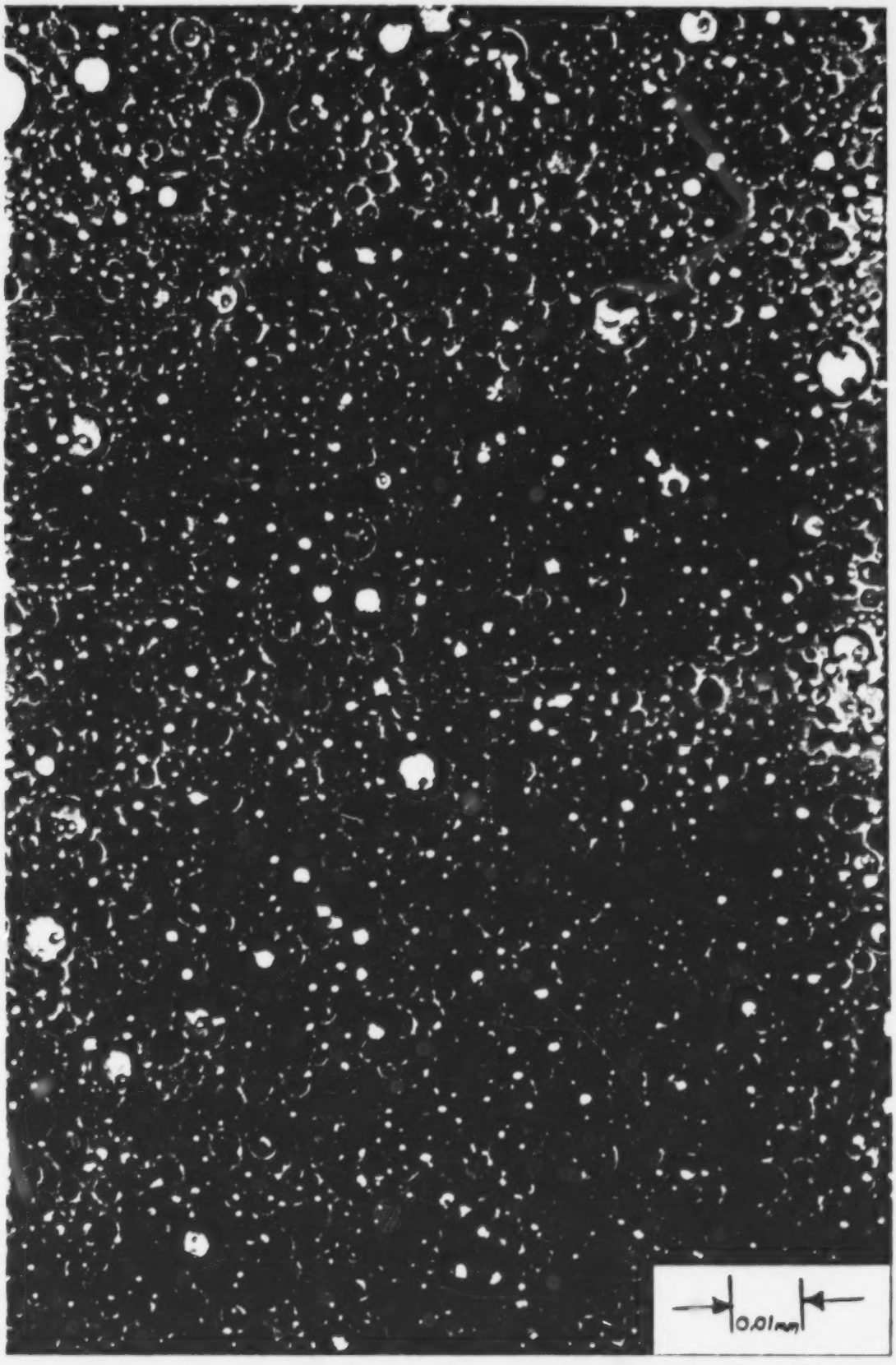

Figure 11: Micrograph of the Westmin, Lindberg Emulsion

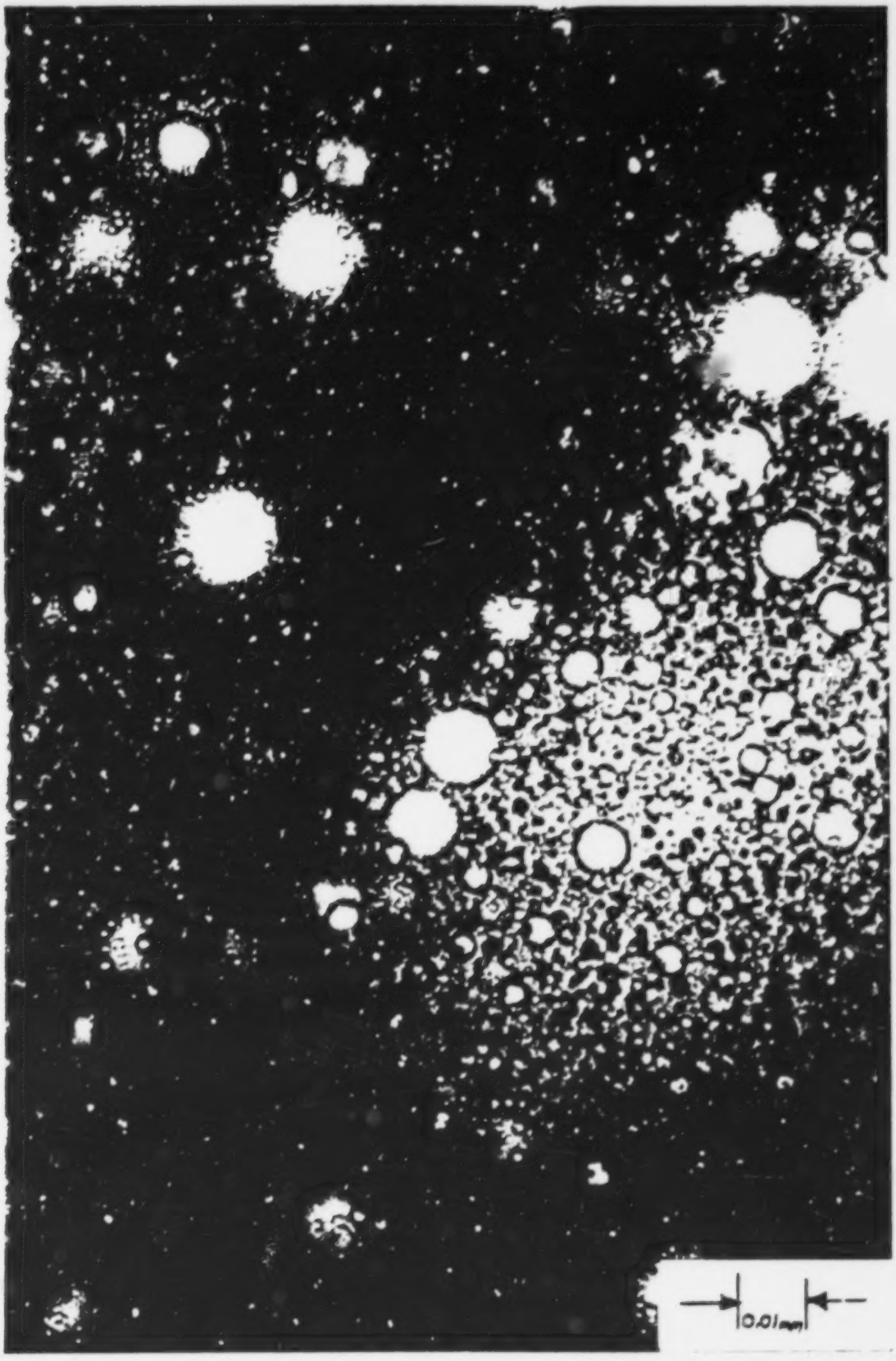

Figure 12: Micrograph of the PanCanadian Lindberg Emulsion

Figure 13: Micrograph of the Texaco Frog Lake Emulsion

4.2 MEASUREMENTS OF RHEOLOGICAL PROPERTIES

4.2.1 Petro-Canada (PCEJ) Athabasca Emulsion:

This sample was provided by Petro-Canada from their PCEJ pilot. The sample was from a well under steam stimulation. The well head sample was a mixture of free water and water-in-oil emulsion. The emulsion appeared to be very stable and highly viscous. Figures 14 shows its shear stress vs shear rate relationship at 28.8°C. As is evident from the curvature in the plot, the emulsion was mildly shear thinning. The corresponding apparent viscosity vs shear rate relationship is shown in Figure 15. As the shear rate increases from 0.7 s^{-1} to 2.5 s^{-1} the viscosity decreases from 105,000 mPa.s to 88,000 mPa.s. Surprisingly, the viscosity versus shear rate curve also shows significant hysteresis effects. The curve is higher in the direction of decreasing shear rates. It is likely that the drop size distribution changes when the shear rate is increased and the viscosities measured in the direction of decreasing shear retain the effects of changed drop size distribution.

Measurements carried out at 49.9°C on the Athabasca sample are shown in Figures 16 and 17. The rheological behaviour was similar to that at 28.8°C except in viscosity hysteresis. At this temperature, the emulsion viscosity was the same in both directions of shear rate change. The rheological behaviour of this emulsion at 70.1°C is shown in figures 18 and 19. At this temperature, the hysteresis reappeared. The smooth lines shown in these figures were drawn by fitting the power law model to the shear stress vs shear rate data. The power law coefficients for this emulsion at three different temperatures are listed in Table 5.

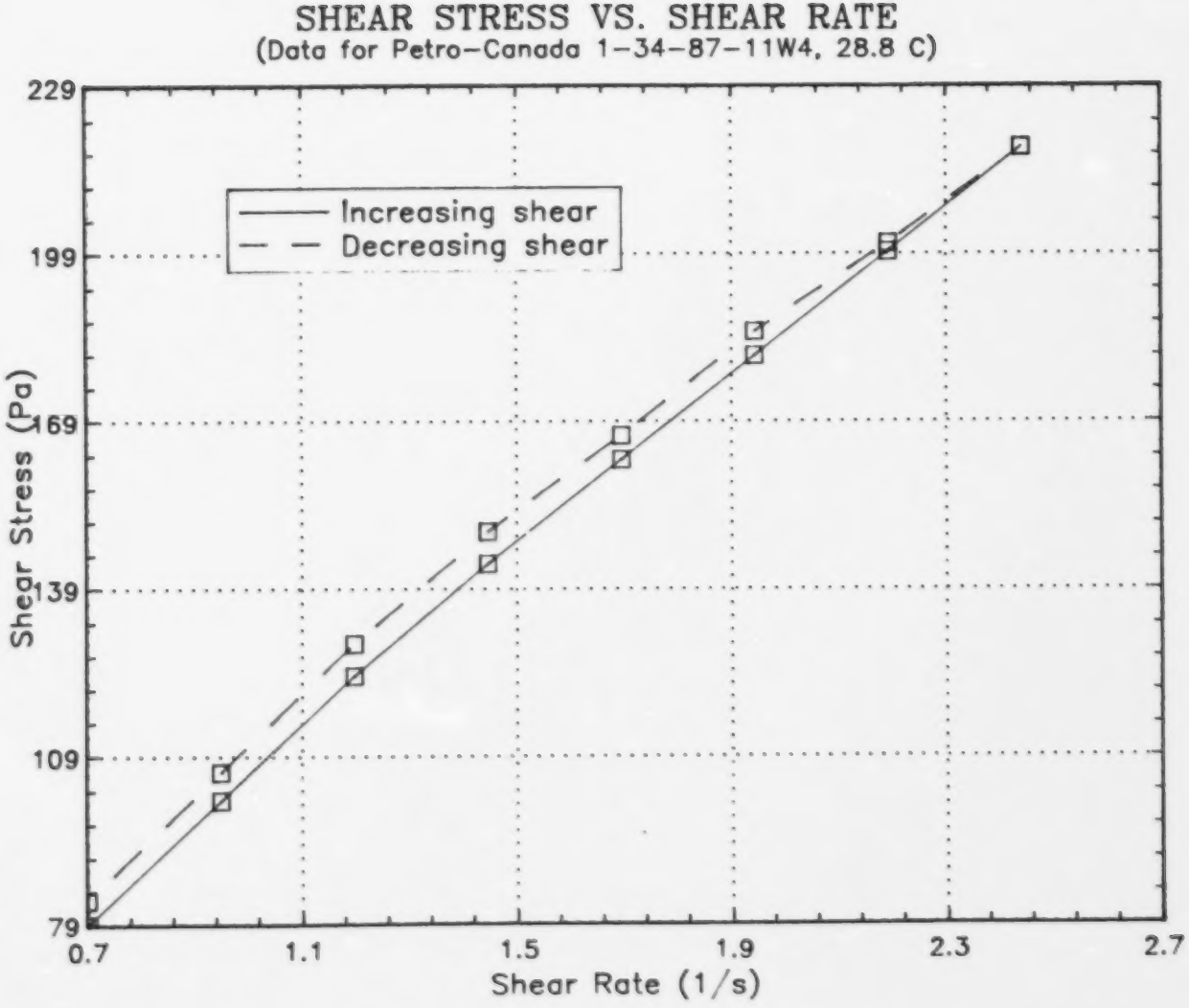
SHEAR STRESS VS. SHEAR RATE
(Data for Petro-Canada 1-34-87-11W4, 28.8 C)
Increasing shear
Decreasing shear
Shear Stress (Pa)
229
199
169
139
109
79
0.7
1.1
1.5
1.9
2.3
2.7
Shear Rate (1/s)

FIGURE 14

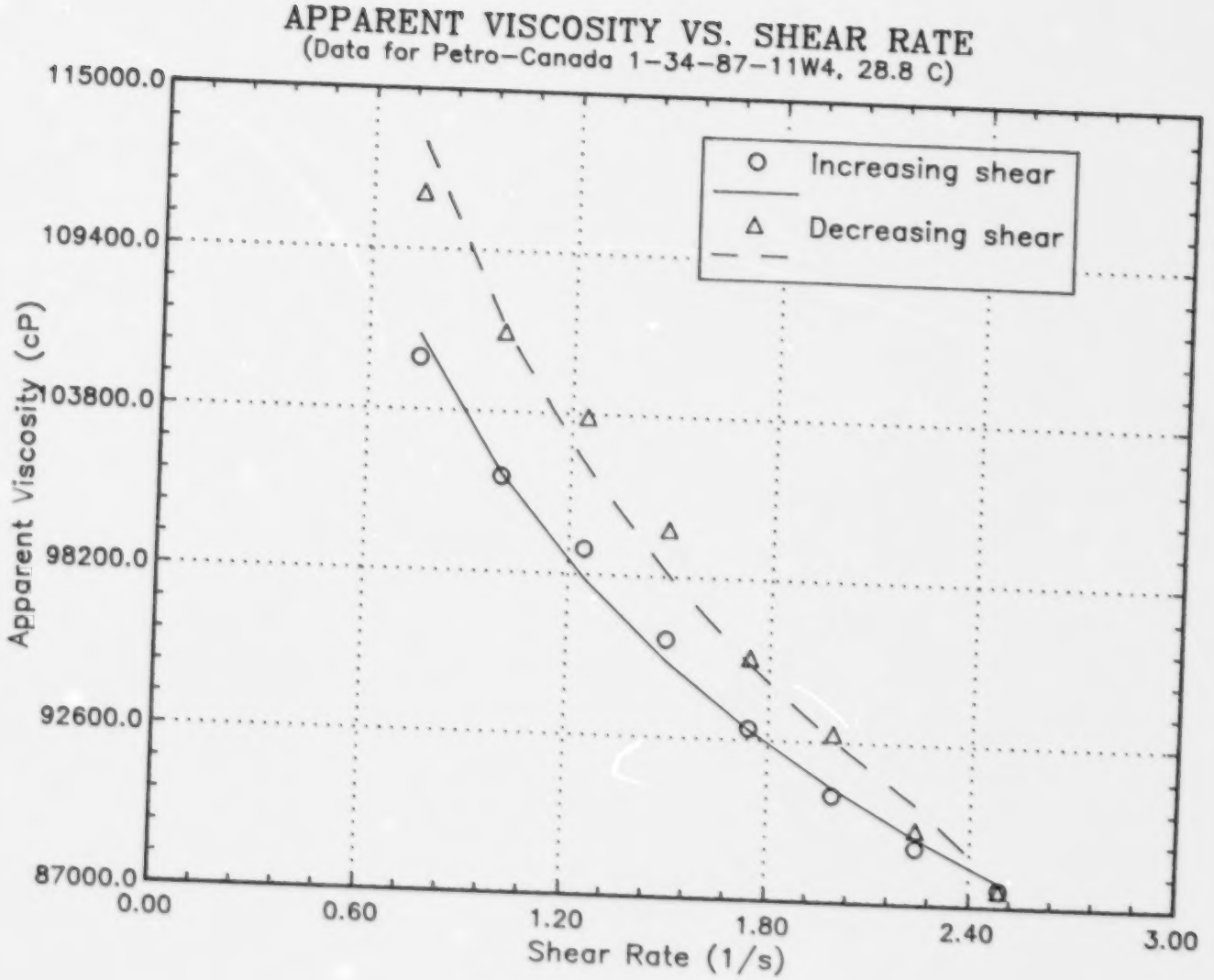
APPARENT VISCOSITY VS. SHEAR RATE
(Data for Petro-Canada 1-34-87-11W4, 28.8 C)
115000.0
109400.0
103800.0
98200.0
92600.0
87000.0
Apparent Viscosity (cP)
0.00
0.60
1.20
1.80
2.40
3.00
Shear Rate (1/s)
Increasing shear
Decreasing shear

FIGURE 15

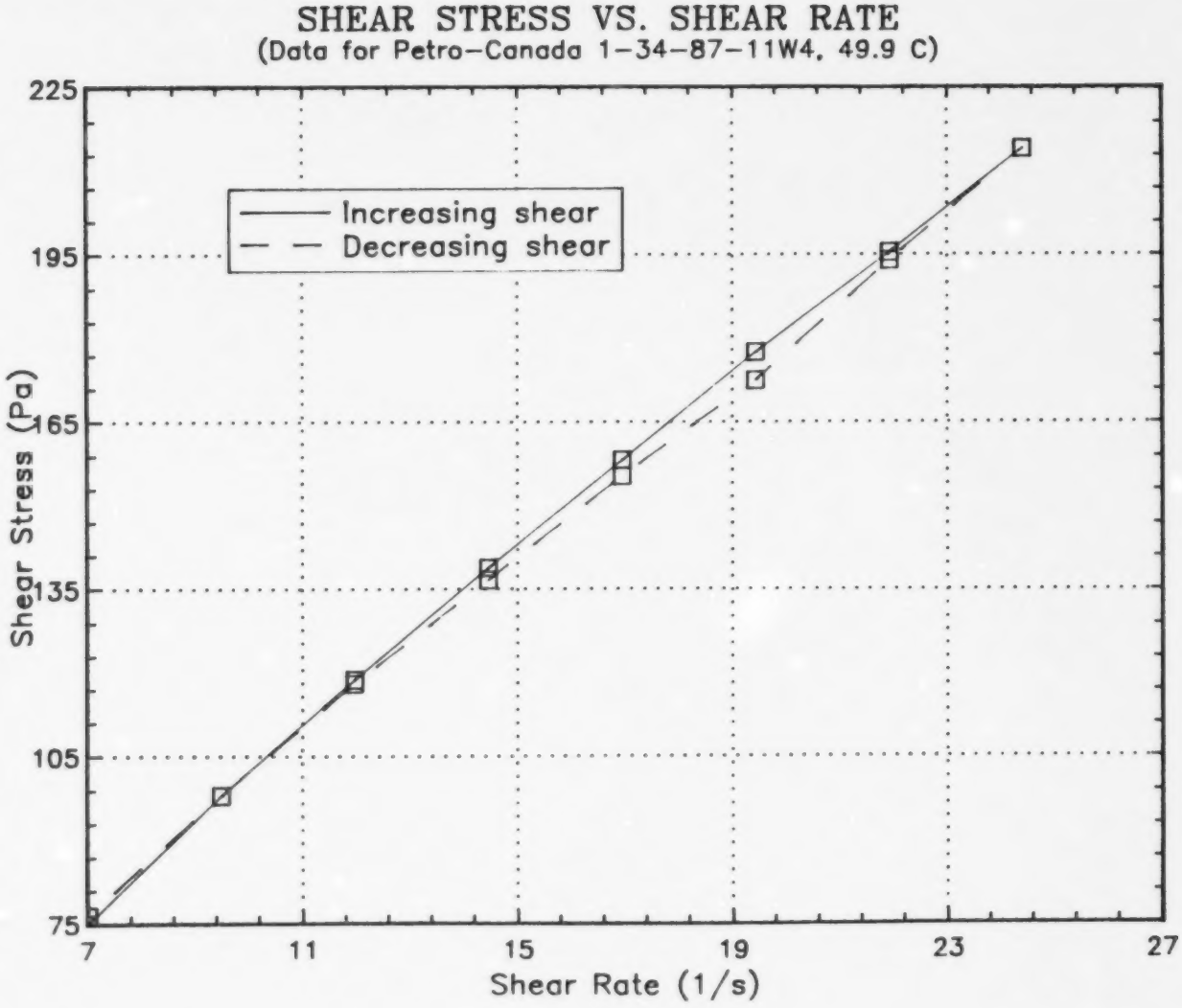
SHEAR STRESS VS. SHEAR RATE
(Data for Petro-Canada 1-34-87-11W4, 49.9 C)
Increasing shear
Decreasing shear
Shear Stress (Pa)
225
195
165
135
105
75
7
11
15
19
23
27
Shear Rate (1/s)

FIGURE 16

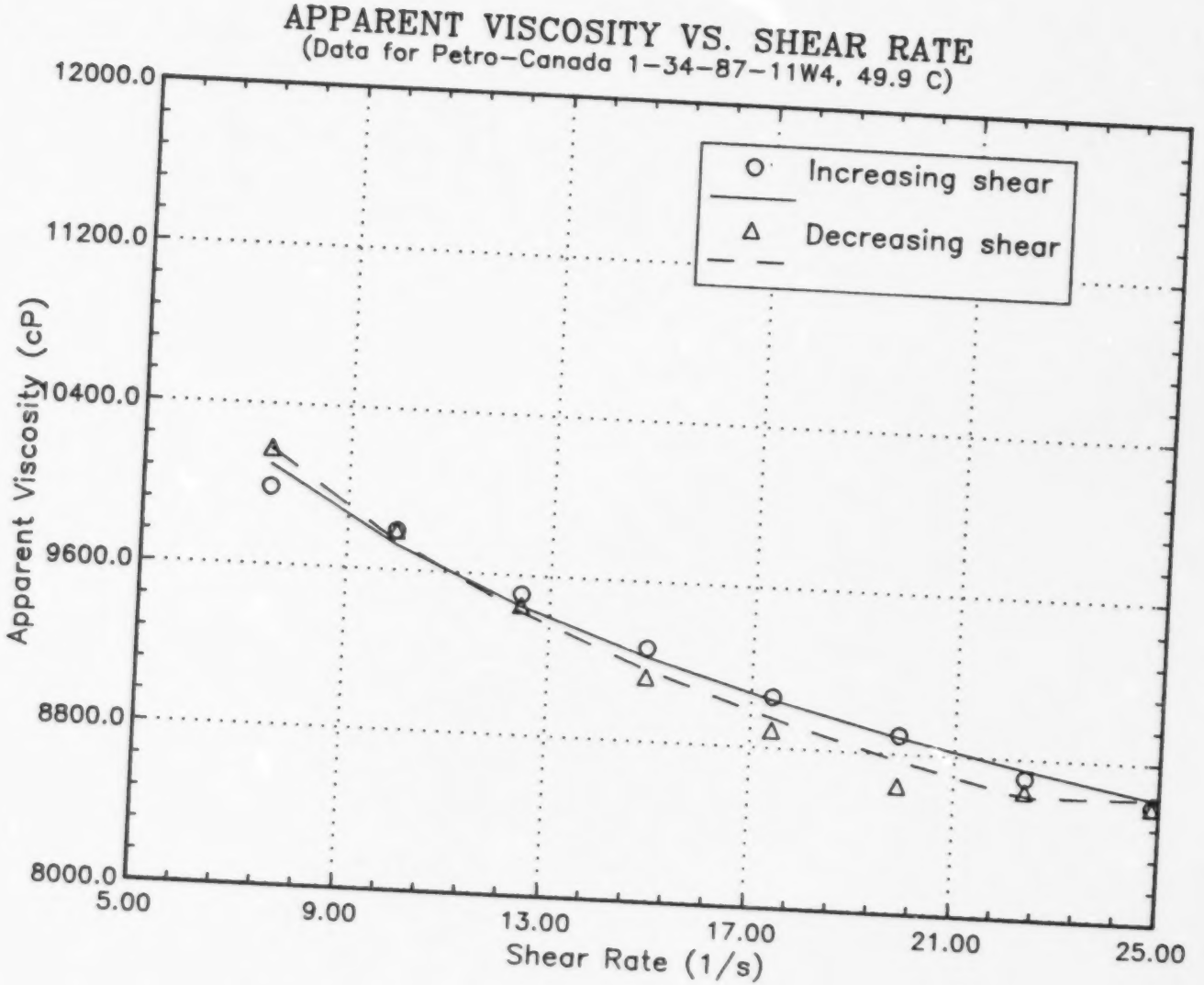
APPARENT VISCOSITY VS. SHEAR RATE
(Data for Petro-Canada 1-34-87-11W4, 49.9 C)
Increasing shear
Decreasing shear
Apparent Viscosity (cP)
12000.0
11200.0
10400.0
9600.0
8800.0
8000.0
5.00
9.00
13.00
17.00
21.00
25.00
Shear Rate (1/s)

FIGURE 17

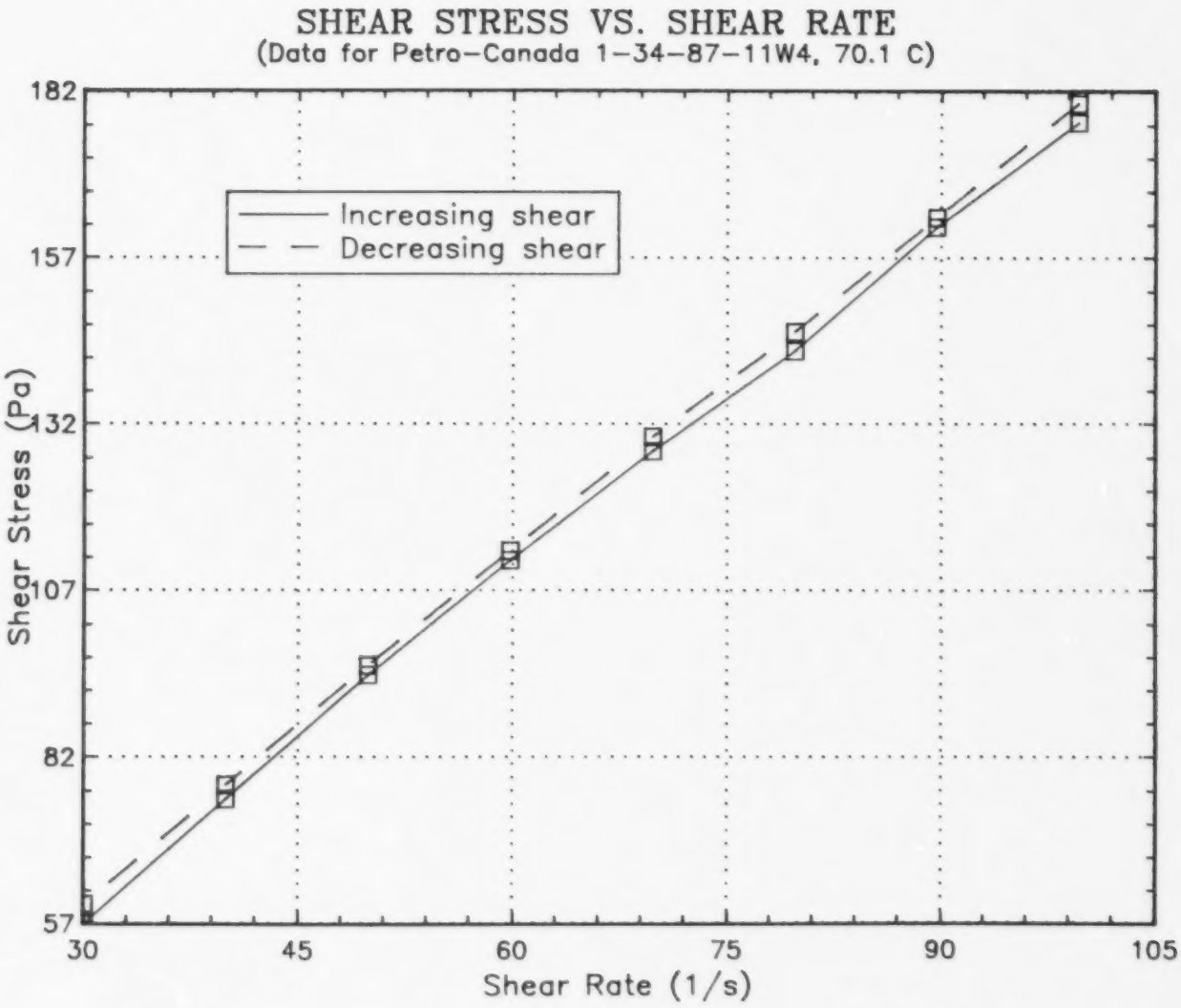
SHEAR STRESS VS. SHEAR RATE
(Data for Petro-Canada 1-34-87-11W4, 70.1 C)
Increasing shear
Decreasing shear
Shear Stress (Pa)
182
157
132
107
82
57
30
45
60
75
90
105
Shear Rate (1/s)

FIGURE 18

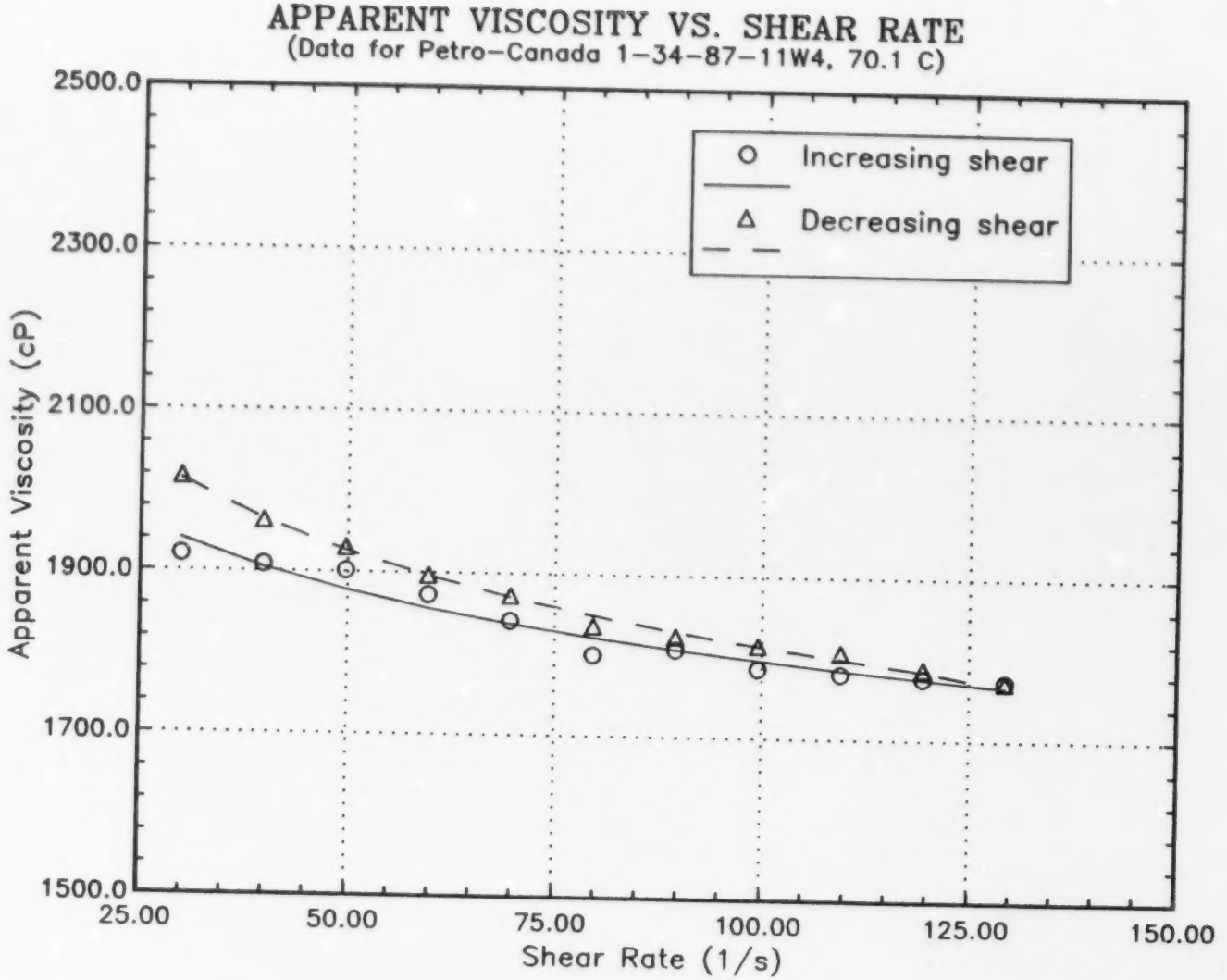
APPARENT VISCOSITY VS. SHEAR RATE
(Data for Petro-Canada 1-34-87-11W4, 70.1 C)
Increasing shear
Decreasing shear
Apparent Viscosity (cP)
2500.0
2300.0
2100.0
1900.0
1700.0
1500.0
25.00
50.00
75.00
100.00
125.00
150.00
Shear Rate (1/s)

FIGURE 19

Table 5: Power Law Coefficients for the Athabasca Emulsion.

Temperature (°C)	Power Law Coefficient for Increasing Shear rate	Power Law Coefficient for Decreasing Shear rate
28.8	0.8405	0.7963
49.9	0.8691	0.8479
70.1	0.9359	0.9131

Increasing temperature appears to reduce the extent of deviation from Newtonian behaviour. It should be mentioned that different shear rate ranges were used at different temperatures. This was necessary due to limitations of the available equipment. The rheometer can only be operated within certain limits of shear stress and rotational speed. At lower temperature the viscosity is high and the shear stress reaches its upper limit at a lower shear rate. At high temperature, the viscosity is low and high rotational speeds (therefore high shear rates) are required to develop measurable shear stresses. Therefore the observed effect of temperature also includes an effect of increased shear rate.

4.2.2 PanCanadian Lindbergh Emulsion:

The flow curve measurements for this emulsion were conducted at 22°C, 41°C, and 61.5°C and these measurements were repeated on two subsequent days. Thus the emulsion was tested at all three temperatures and left in the rheometer overnight. Next day the same measurements were repeated, followed by aging overnight in the rheometer and repeat measurements on the third day. The shear stress versus shear rate behaviour at 22°C is shown in Figure 20.

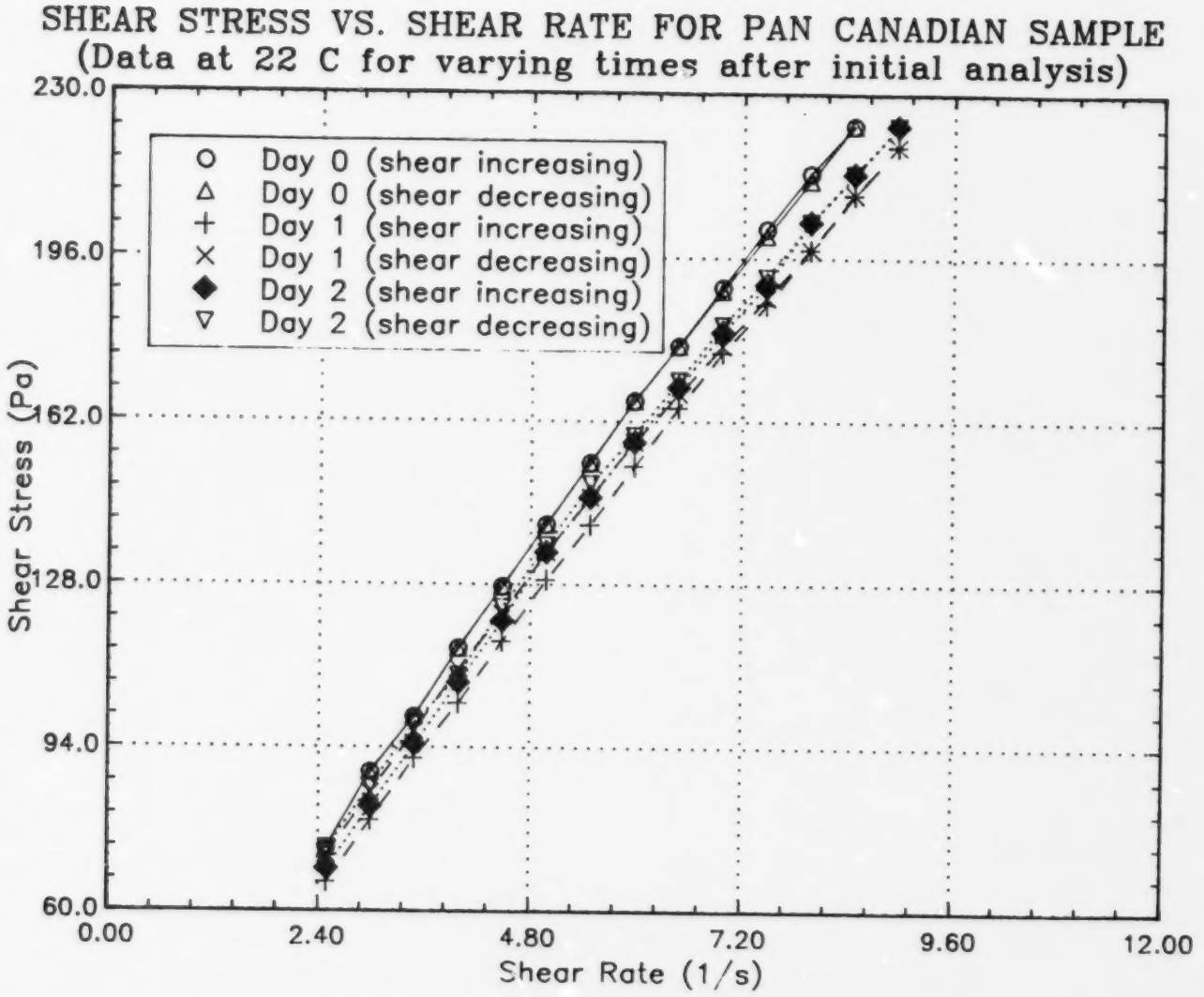
SHEAR STRESS VS. SHEAR RATE FOR PAN CANADIAN SAMPLE
(Data at 22 C for varying times after initial analysis)
Day 0 (shear increasing)
Day 0 (shear decreasing)
Day 1 (shear increasing)
Day 1 (shear decreasing)
Day 2 (shear increasing)
Day 2 (shear decreasing)
Shear Stress (Pa)
230.0
196.0
162.0
128.0
94.0
60.0
0.00
2.40
4.80
7.20
9.60
12.00
Shear Rate (1/s)

FIGURE 20

The curves for the sample aged for one day are shifted downward and show increased hysteresis. The third days measurements (sample aged for 2 days) fall in between the first two. This can be seen more clearly in Figure 21 which shows the apparent viscosity vs shear rate results. The results at higher temperatures are shown in figures 22 to 25.

The reasons for observed change in behaviour with time were not investigated. Most probably a change in emulsion drop size distribution resulting from the effects of changes in shear rate and temperature is involved. It is also conceivable that the emulsion looses some water at higher temperatures and this water becomes re-emulsified during the next days measurements. It should be stressed that these changes are generally within 10% of the apparent viscosity and only minor change in emulsion characteristics may be involved. The power law coefficients for these emulsions are listed in Table 6. This emulsion was less non-Newtonian than the Athabasca emulsion. Changes in the power law coefficient with temperature and time were within ±3.5% of the average and may be considered insignificant.

The effect of pressure on emulsion rheology was also investigated (by conducting measurements at three different pressures). Results are shown in figures 26 to 29. As expected the viscosity at a given shear rate increased with increasing pressure. Other than this, the pressure appeared to have very little effect on the emulsion properties. As shown in Table 7 the power law coefficient remained unchanged with pressure.

APPARENT VISCOSITY VS. SHEAR RATE FOR PAN CANADIAN SAMPLE
(Data at 22 C for varying times after initial analysis)

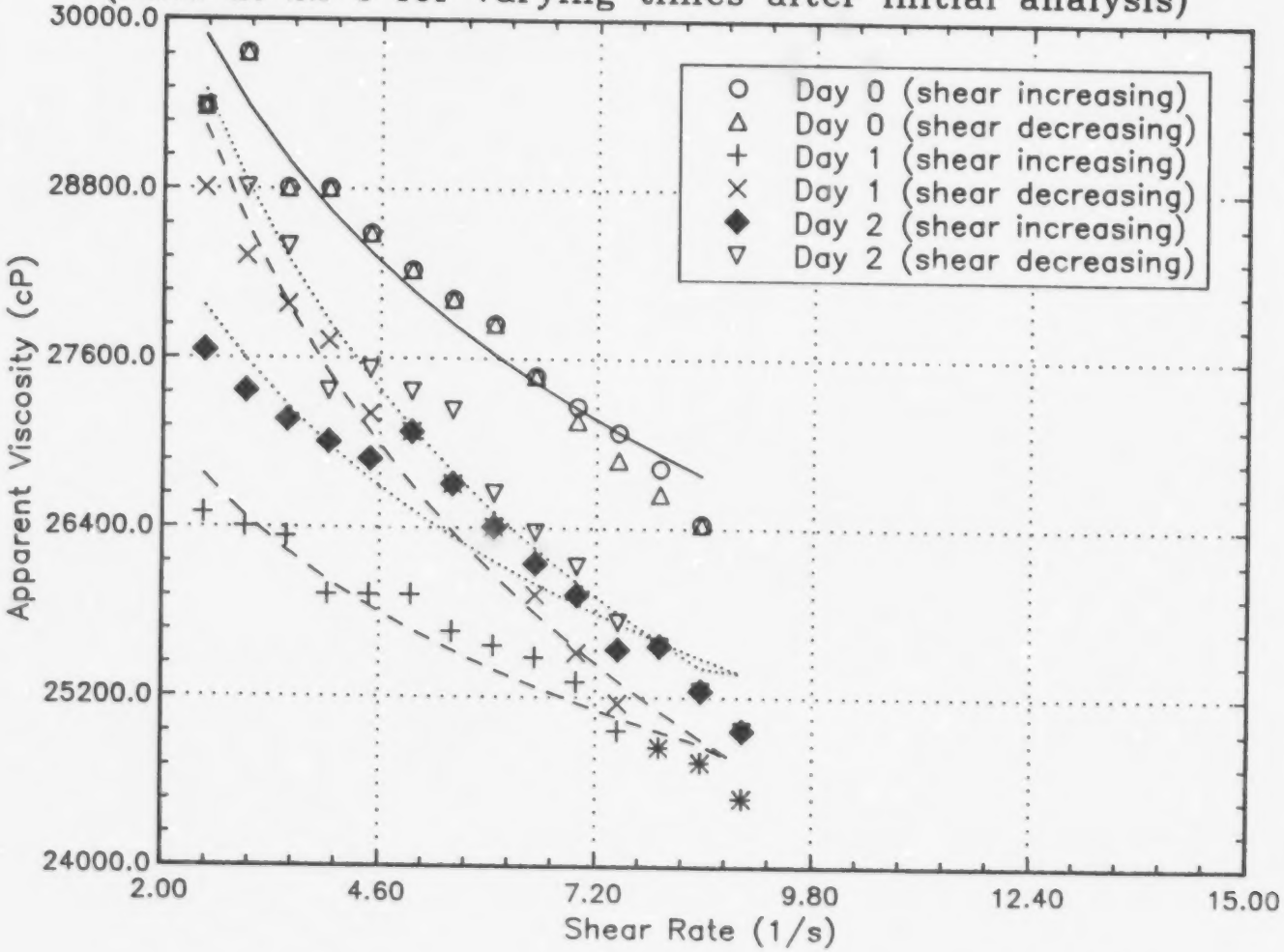

FIGURE 21

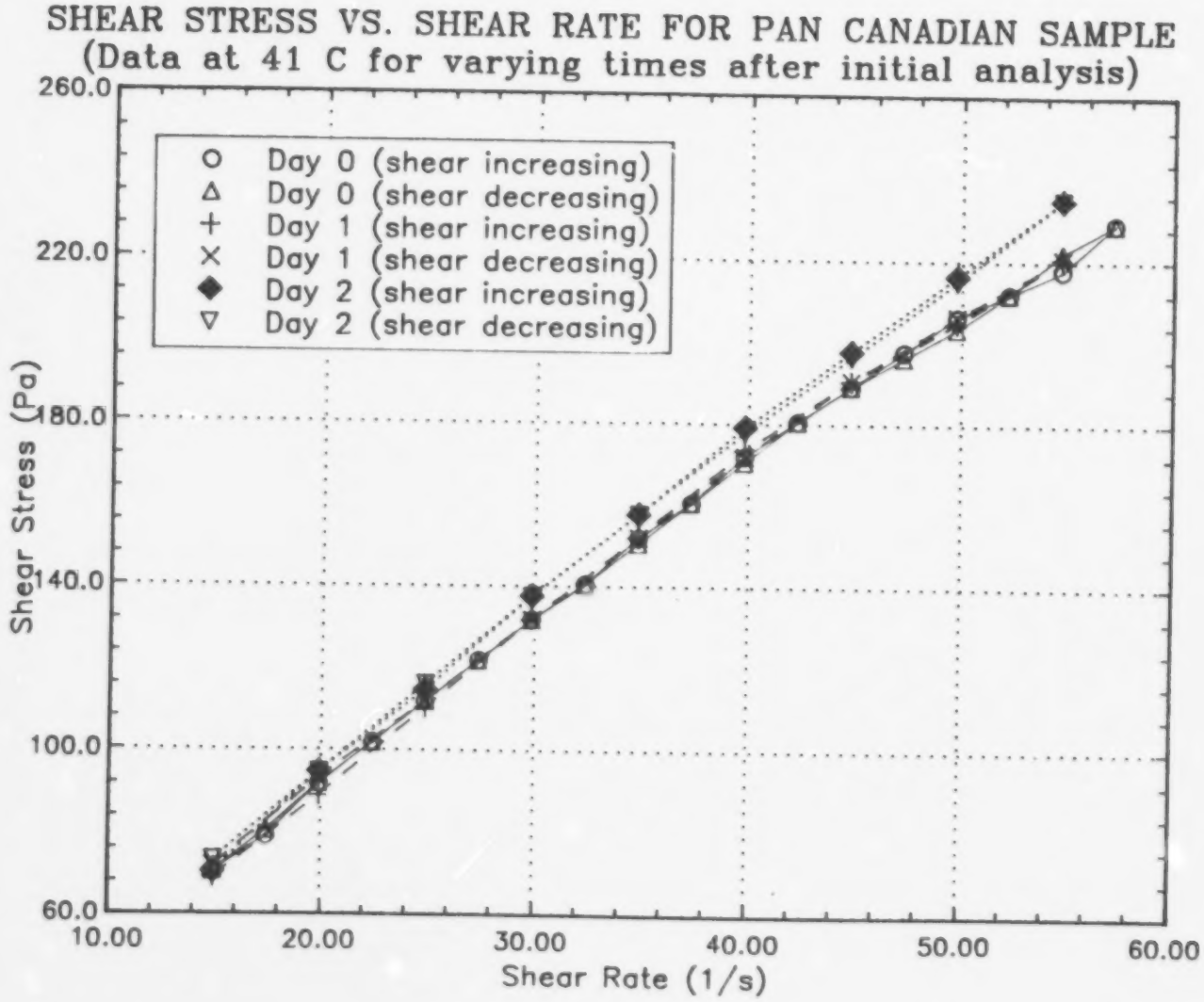
SHEAR STRESS VS. SHEAR RATE FOR PAN CANADIAN SAMPLE
(Data at 41 C for varying times after initial analysis)
Day 0 (shear increasing)
Day 0 (shear decreasing)
Day 1 (shear increasing)
Day 1 (shear decreasing)
Day 2 (shear increasing)
Day 2 (shear decreasing)
Shear Stress (Pa)
260.0
220.0
180.0
140.0
100.0
60.0
10.00
20.00
30.00
40.00
50.00
60.00
Shear Rate (1/s)

FIGURE 22

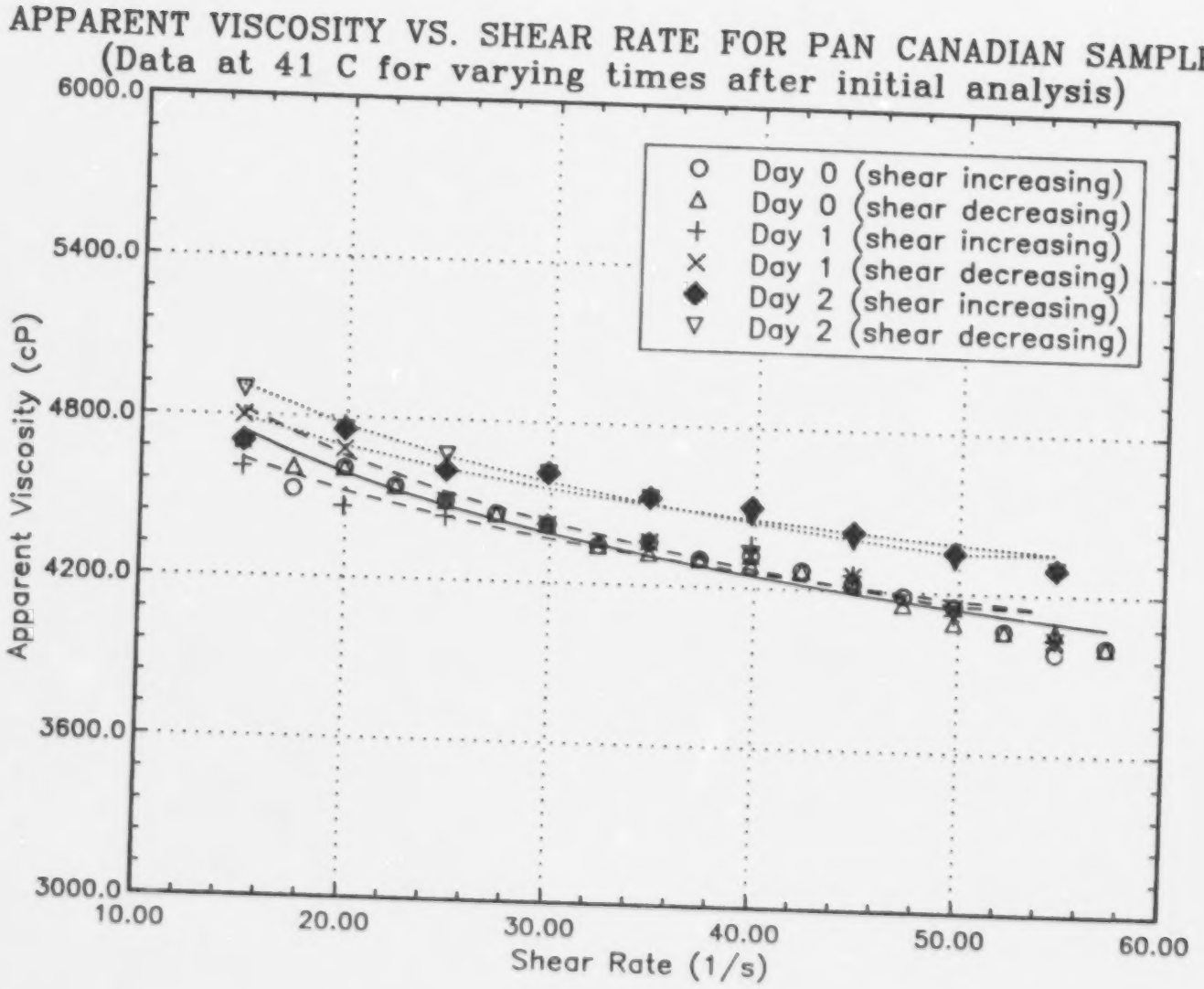
APPARENT VISCOSITY VS. SHEAR RATE FOR PAN CANADIAN SAMPLE
(Data at 41 C for varying times after initial analysis)
Day 0 (shear increasing)
Day 0 (shear decreasing)
Day 1 (shear increasing)
Day 1 (shear decreasing)
Day 2 (shear increasing)
Day 2 (shear decreasing)
Apparent Viscosity (cP)
6000.0
5400.0
4800.0
4200.0
3600.0
3000.0
10.00
20.00
30.00
40.00
50.00
60.00
Shear Rate (1/s)

FIGURE 23

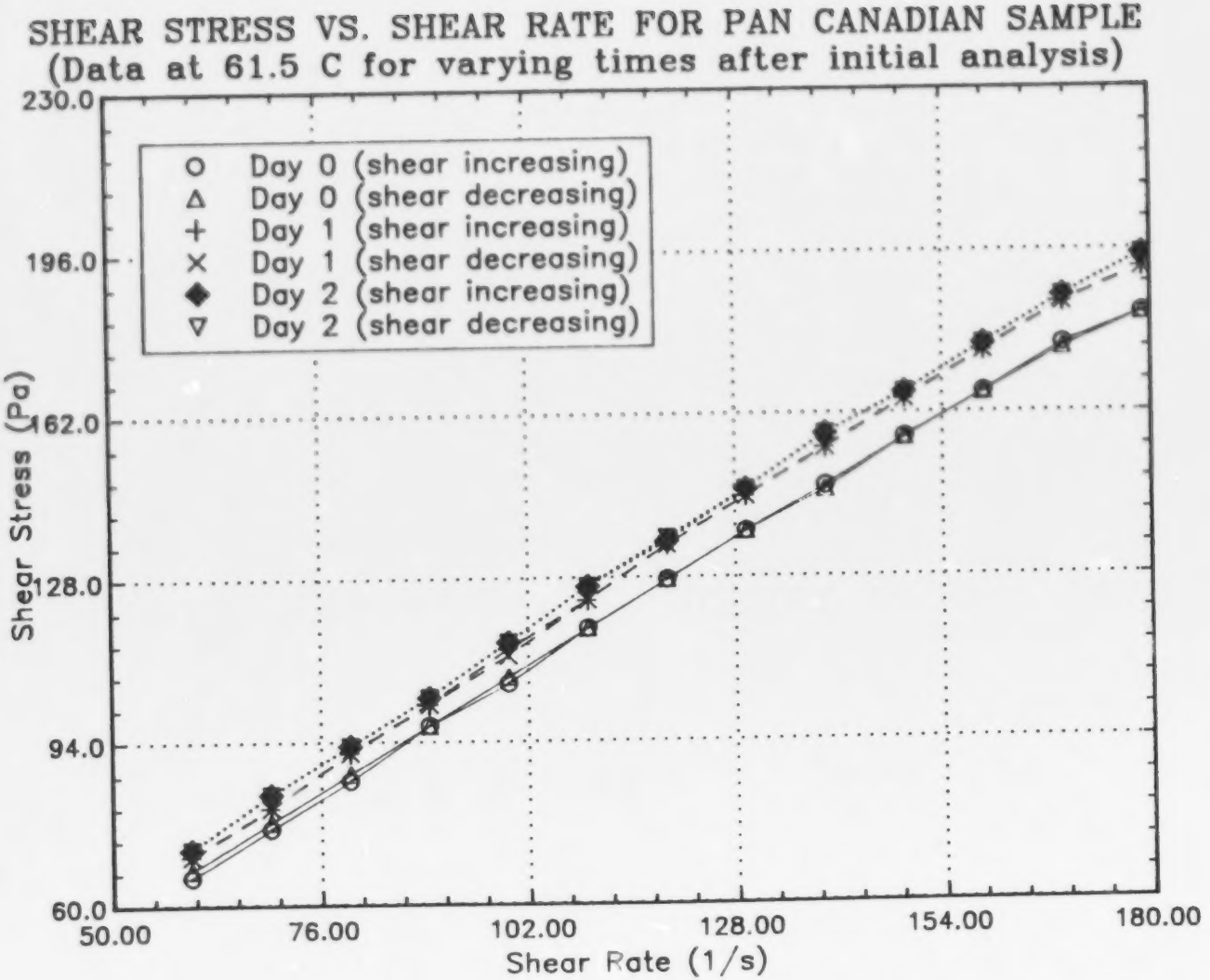
SHEAR STRESS VS. SHEAR RATE FOR PAN CANADIAN SAMPLE
(Data at 61.5 C for varying times after initial analysis)
Day 0 (shear increasing)
Day 0 (shear decreasing)
Day 1 (shear increasing)
Day 1 (shear decreasing)
Day 2 (shear increasing)
Day 2 (shear decreasing)
Shear Stress (Pa)
230.0
196.0
162.0
128.0
94.0
60.0
50.00
76.00
102.00
128.00
154.00
180.00
Shear Rate (1/s)

FIGURE 24

APPARENT VISCOSITY VS. SHEAR RATE FOR PAN CANADIAN SAMPLE
(Data at 61 C for varying times after initial analysis)

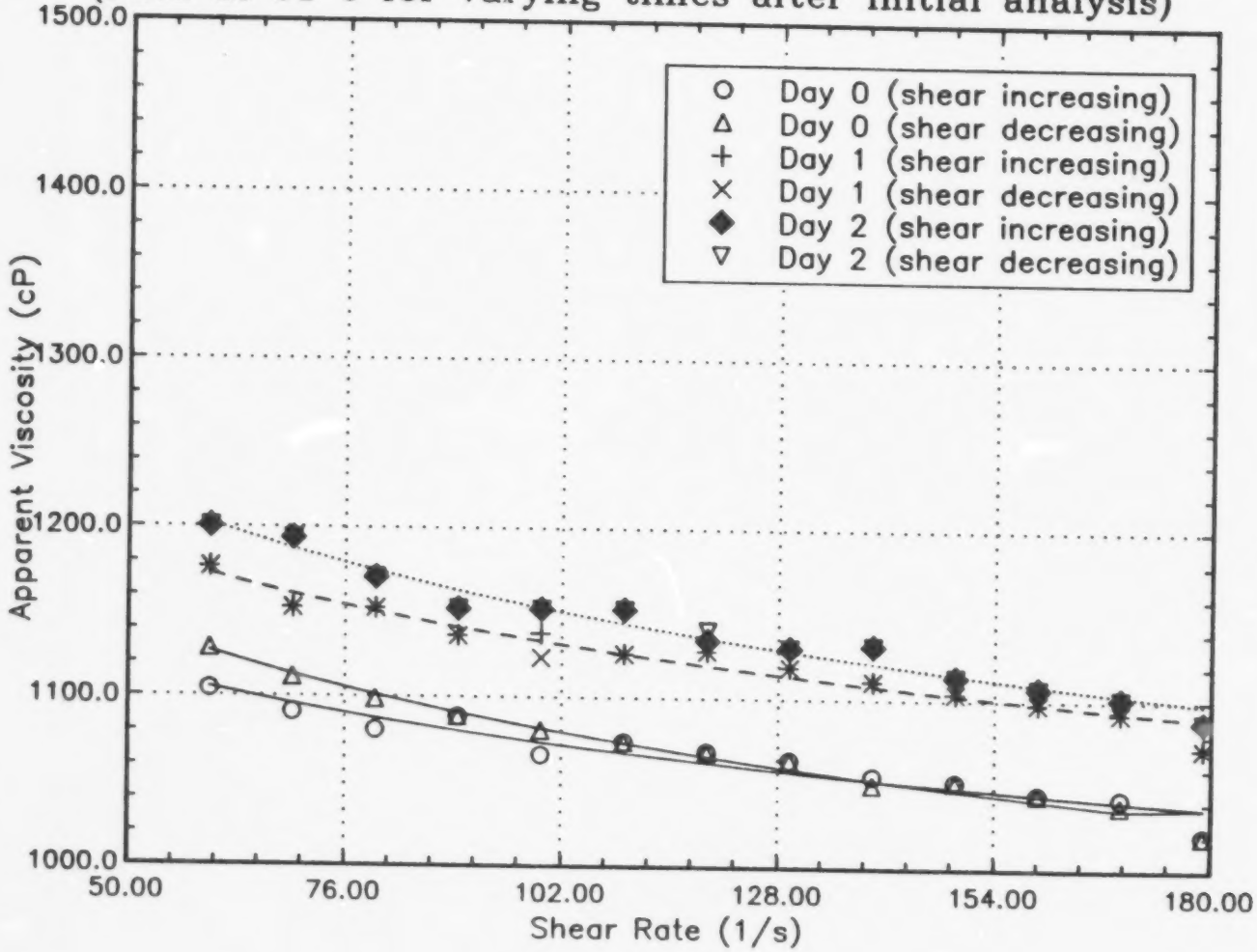

FIGURE 25

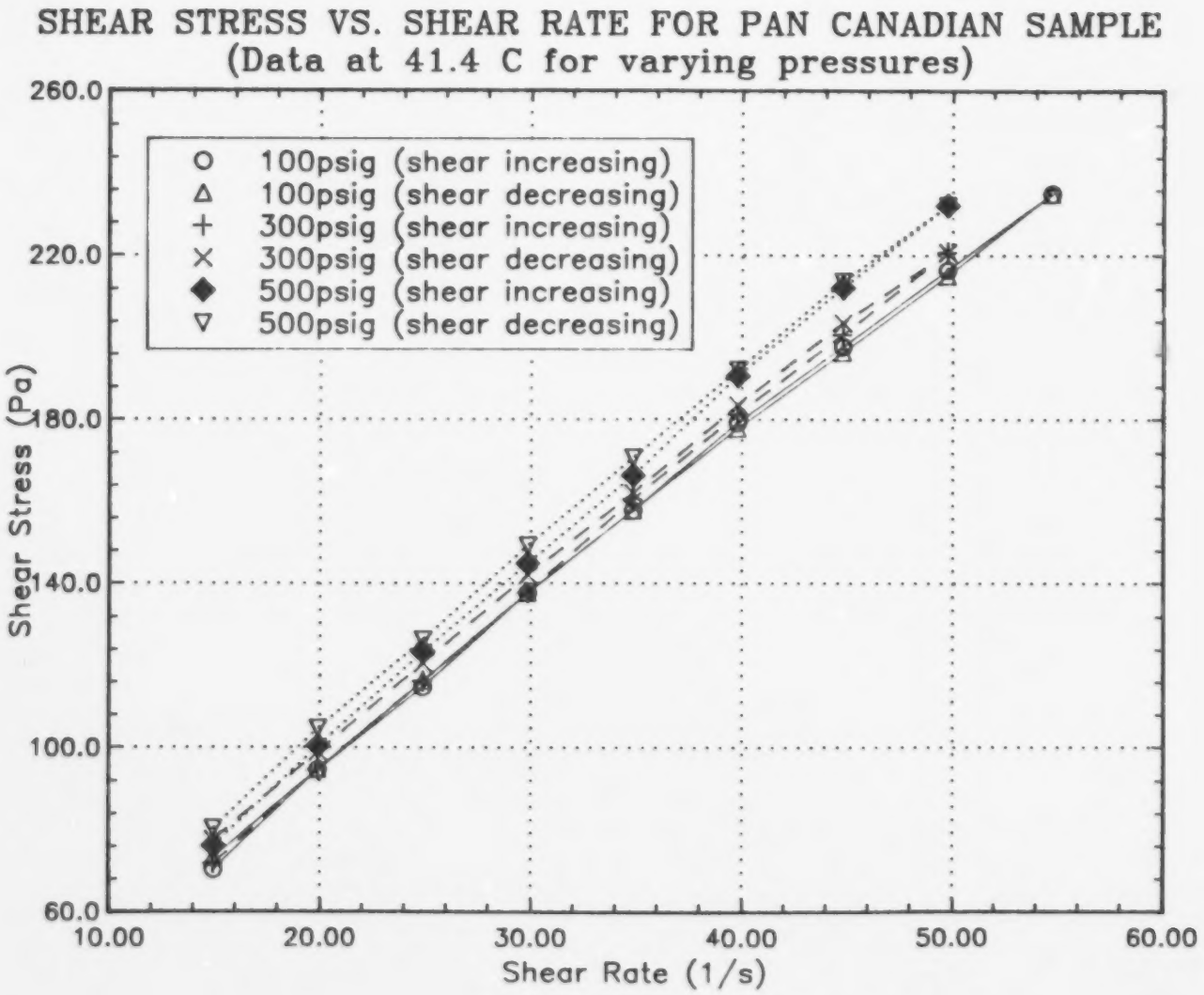
SHEAR STRESS VS. SHEAR RATE FOR PAN CANADIAN SAMPLE
(Data at 41.4 C for varying pressures)
100psig (shear increasing)
100psig (shear decreasing)
300psig (shear increasing)
300psig (shear decreasing)
500psig (shear increasing)
500psig (shear decreasing)
Shear Stress (Pa)
260.0
220.0
180.0
140.0
100.0
60.0
10.00
20.00
30.00
40.00
50.00
60.00
Shear Rate (1/s)

FIGURE 26

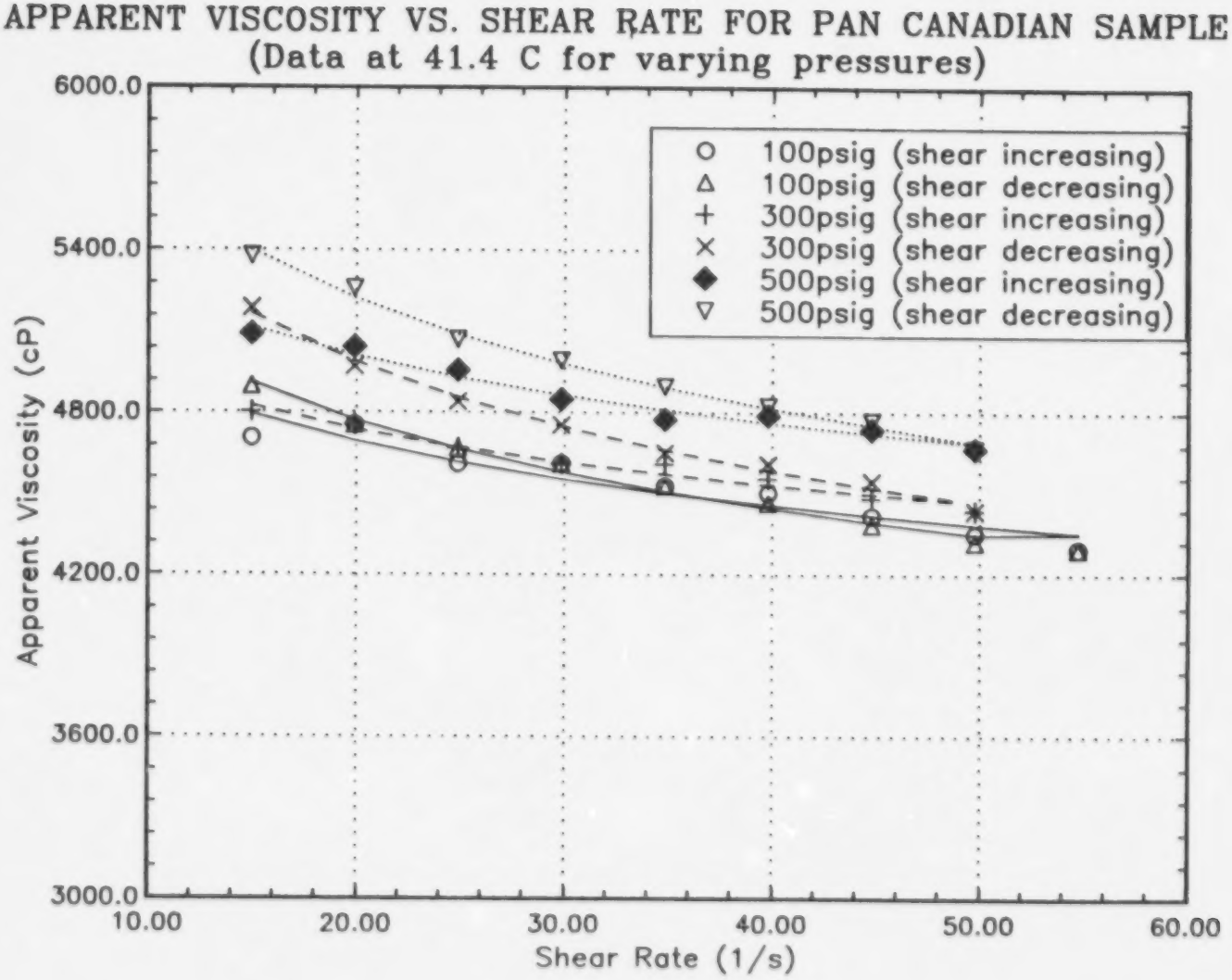
APPARENT VISCOSITY VS. SHEAR RATE FOR PAN CANADIAN SAMPLE
(Data at 41.4 C for varying pressures)
6000.0
5400.0
4800.0
4200.0
3600.0
3000.0
Apparent Viscosity (cP)
10.00
20.00
30.00
40.00
50.00
60.00
Shear Rate (1/s)
100psig (shear increasing)
100psig (shear decreasing)
300psig (shear increasing)
300psig (shear decreasing)
500psig (shear increasing)
500psig (shear decreasing)

FIGURE 27

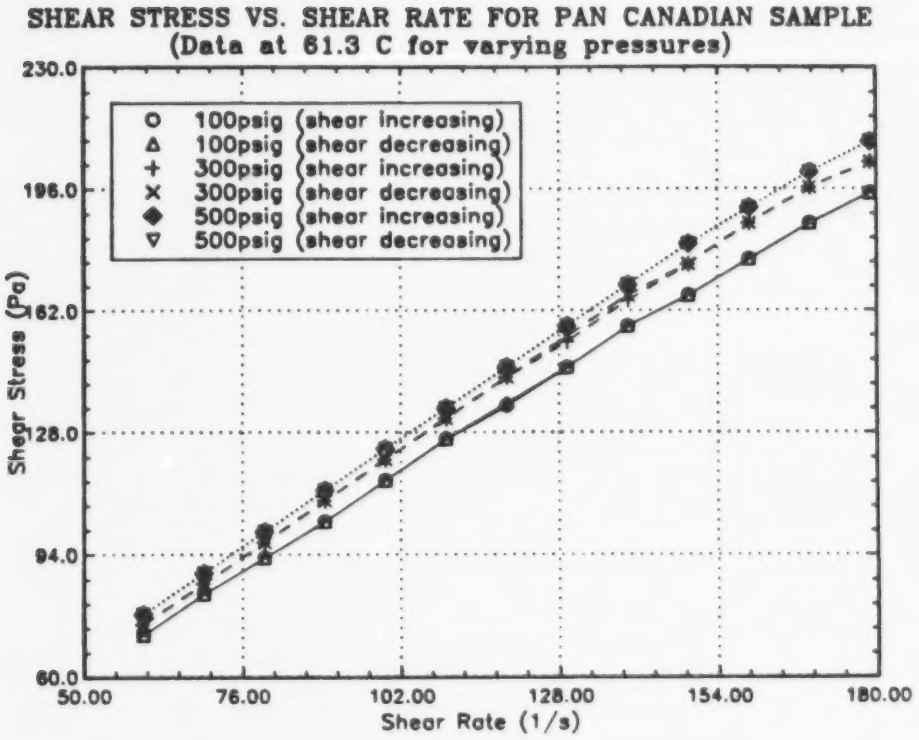

FIGURE 28

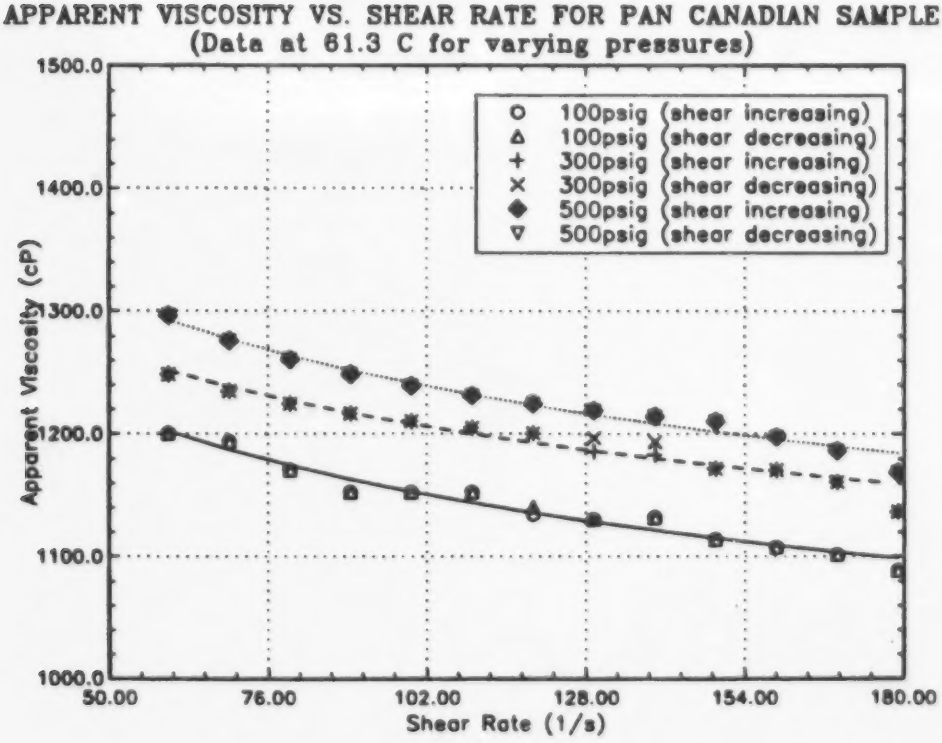

FIGURE 29

Table 6: Power Law Coefficients for the PanCanadian Lindbergh Emulsion

Temperature (°C)	Power Law Coefficient for Increasing Shear rate	Power Law Coefficient for Decreasing Shear rate
Day 0:		
22.2	0.91	0.91
41.3	0.89	0.88
61.7	0.94	0.92
Day 1:		
21.9	0.94	0.87
41.1	0.91	0.88
61.4	0.93	0.93
Day 2:		
22.2	0.92	0.88
41.4	0.93	0.90
61.3	0.92	0.92

Table 7: Effect of Pressure on Power Law Coefficient of PanCanadian Lindbergh Emulsion

Pressure (psig)	Power Law Coefficient for Increasing Shear rate	Power Law Coefficient for Decreasing Shear rate
At 41.4°C:		
100	0.93	0.89
300	0.94	0.88
500	0.93	0.88
At 61.3°C:		
100	0.92	0.92
300	0.93	0.93
500	0.92	0.92

4.2.3 Westmin Lindbergh Emulsion:

The rheological behaviour of this emulsion is compared with two others in figures 30 to 35. This emulsion was found to be totally Newtonian in viscosity behaviour. Within the accuracy of the instrument used, no effect of shear rate on viscosity was detected. Since this emulsion contained only 7.3 weight percent water, it was not expected to be highly non-Newtonian.

4.2.4 Texaco Frog Lake Emulsion:

The behaviour of this emulsion is also shown in figures 30 to 35. This emulsion also showed Newtonian behaviour. In view of the small amount of emulsified water (2.89 wt. percent) present in this emulsion, it is not a surprising result.

4.3 Discussion:

The measurements presented above show that the water-in-oil emulsions can be considerably more viscous than the pure oil phase and the apparent viscosity is higher at low shear rates. Therefore the presence of emulsified water beyond a threshold amount will have a significant effect on the flow of oil. If such emulsions are generated in situ, they can reduce the flow of oil to production wells by increasing the apparent viscosity of the flowing oil. It is apparent that this reduction in well productivity will depend on the volume fraction of emulsified water present, the drop size distribution of the emulsified water as well as on the pore size distribution of the

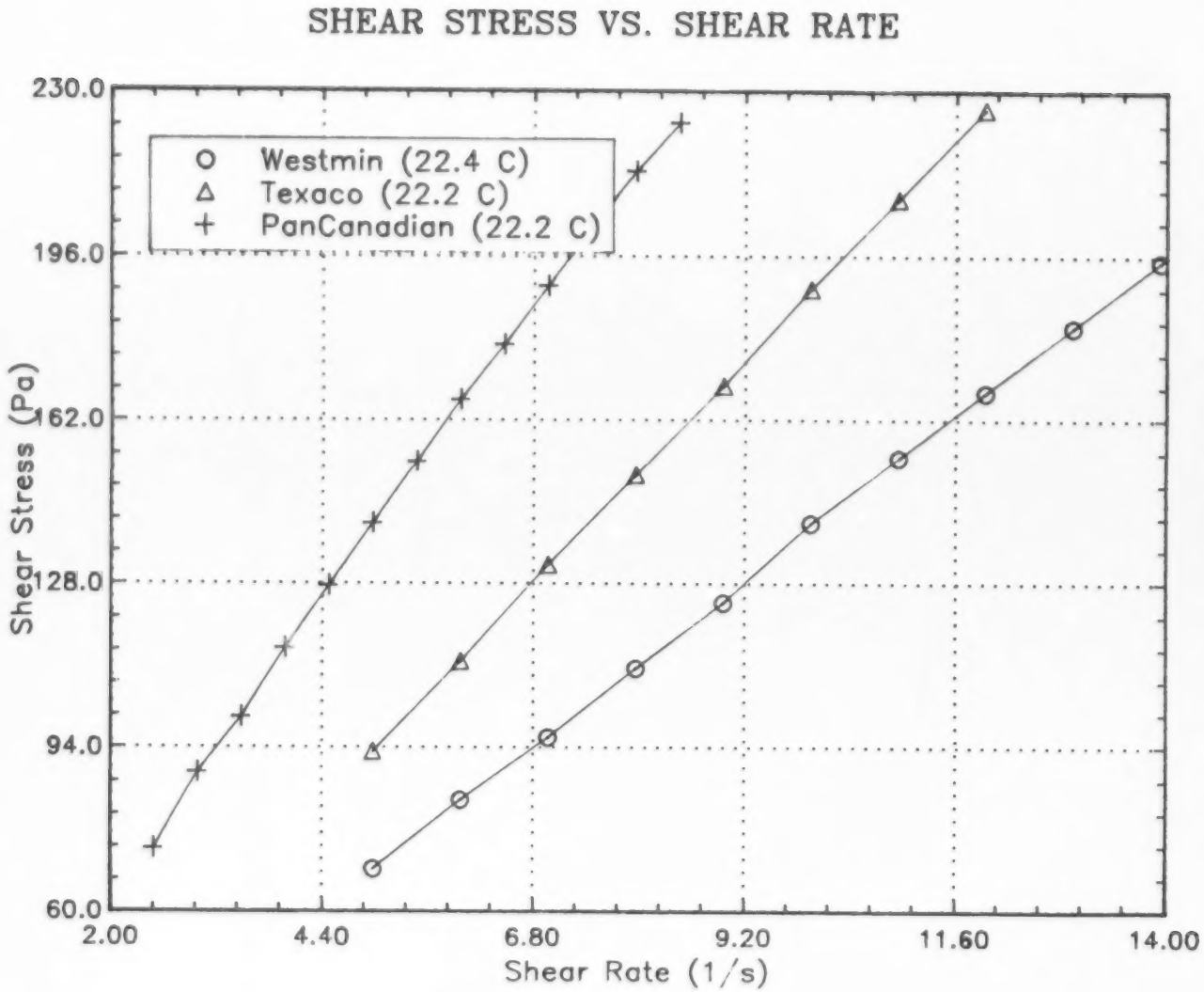
SHEAR STRESS VS. SHEAR RATE
Westmin (22.4 C)
Texaco (22.2 C)
PanCanadian (22.2 C)
Shear Stress (Pa)
230.0
196.0
162.0
128.0
94.0
60.0
2.00
4.40
6.80
9.20
11.60
14.00
Shear Rate (1/s)

FIGURE 30

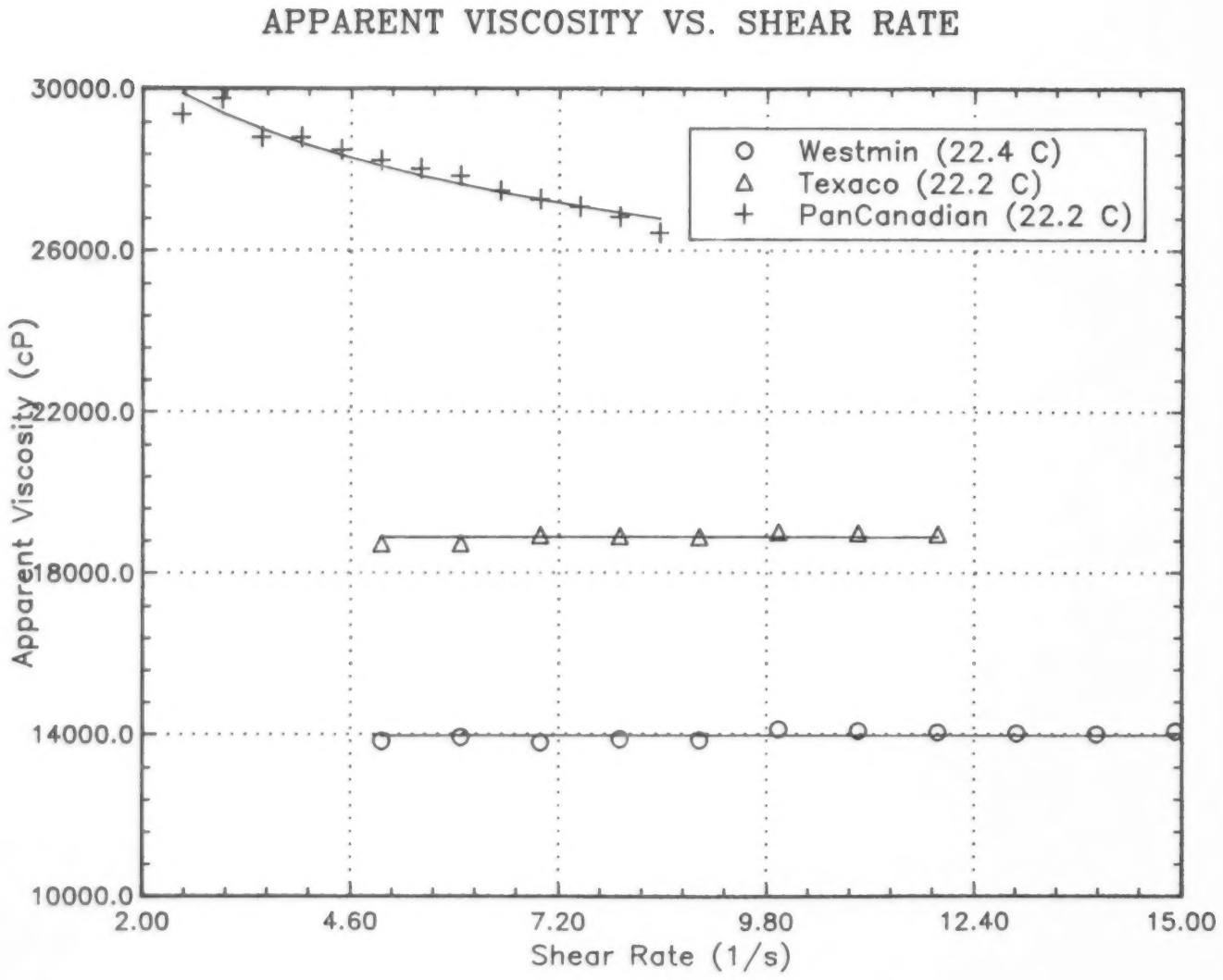
APPARENT VISCOSITY VS. SHEAR RATE
30000.0
26000.0
22000.0
18000.0
14000.0
10000.0
Apparent Viscosity (cP)
2.00
4.60
7.20
9.80
12.40
15.00
Shear Rate (1/s)
Westmin (22.4 C)
Texaco (22.2 C)
PanCanadian (22.2 C)

FIGURE 31

SHEAR STRESS VS. SHEAR RATE

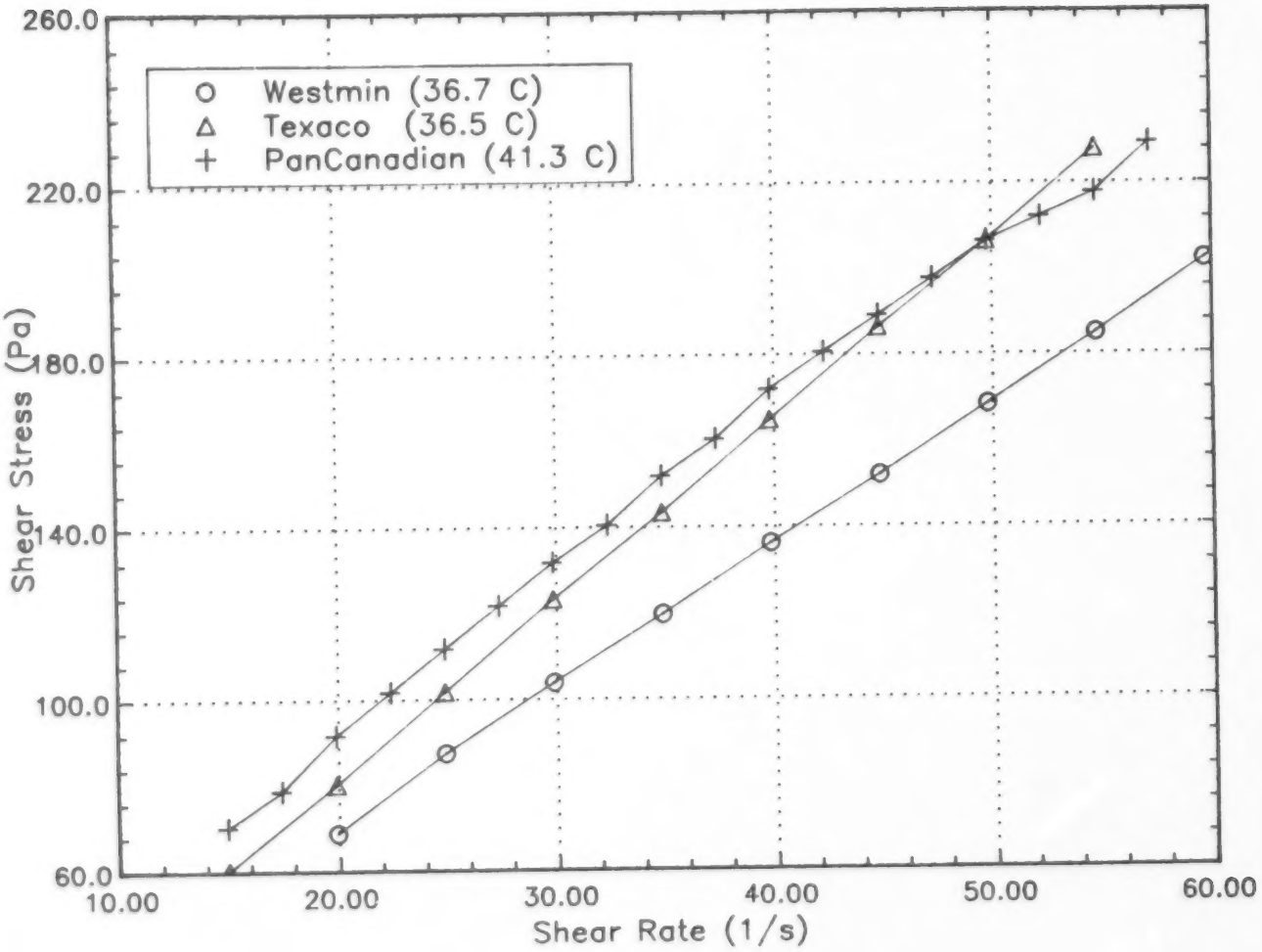

FIGURE 32

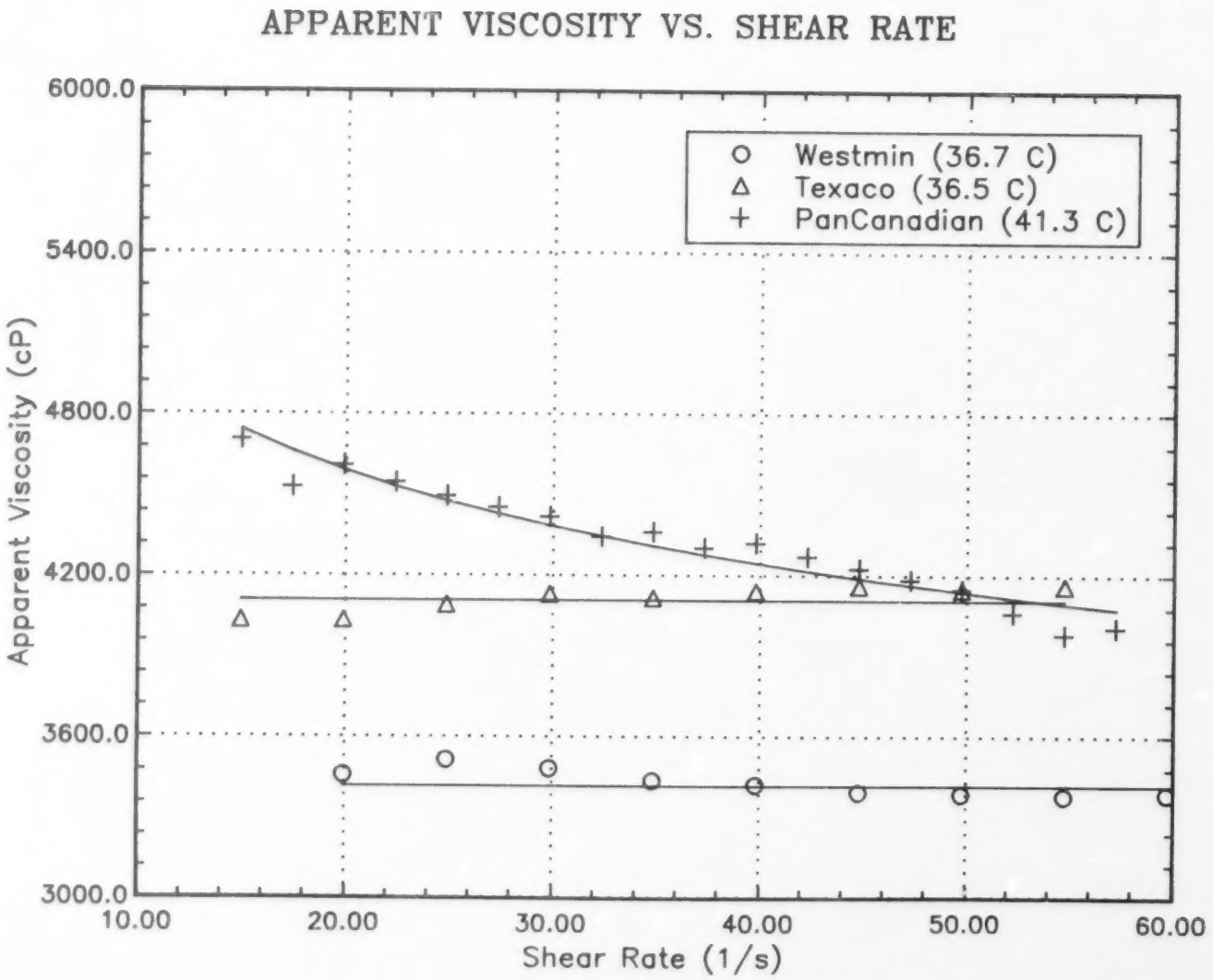
APPARENT VISCOSITY VS. SHEAR RATE
Westmin (36.7 C)
Texaco (36.5 C)
PanCanadian (41.3 C)
Apparent Viscosity (cP)
6000.0
5400.0
4800.0
4200.0
3600.0
3000.0
10.00
20.00
30.00
40.00
50.00
60.00
Shear Rate (1/s)

FIGURE 33

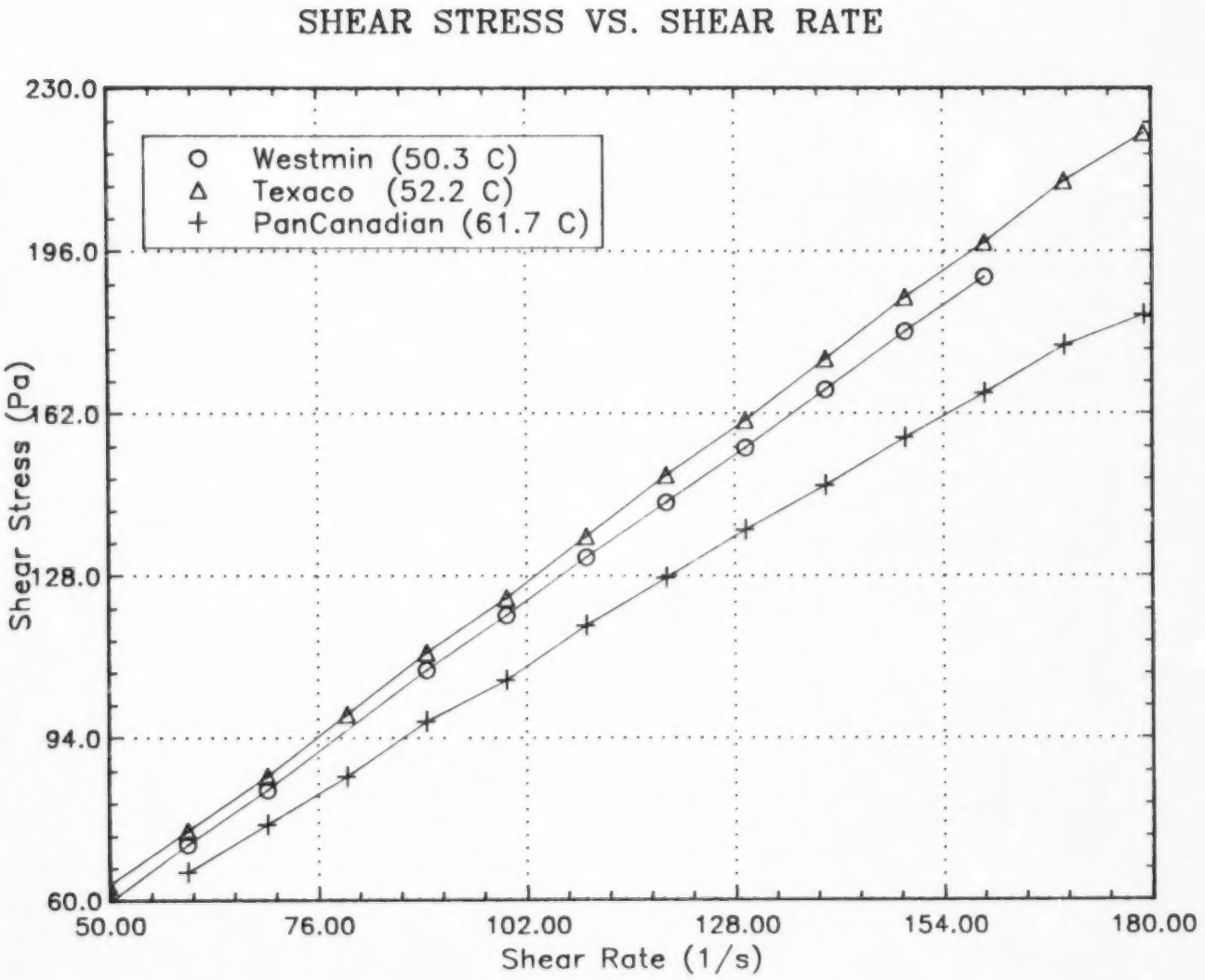
SHEAR STRESS VS. SHEAR RATE
Westmin (50.3 C)
Texaco (52.2 C)
PanCanadian (61.7 C)
Shear Stress (Pa)
230.0
196.0
162.0
128.0
94.0
60.0
50.00
76.00
102.00
128.00
154.00
180.00
Shear Rate (1/s)

FIGURE 34

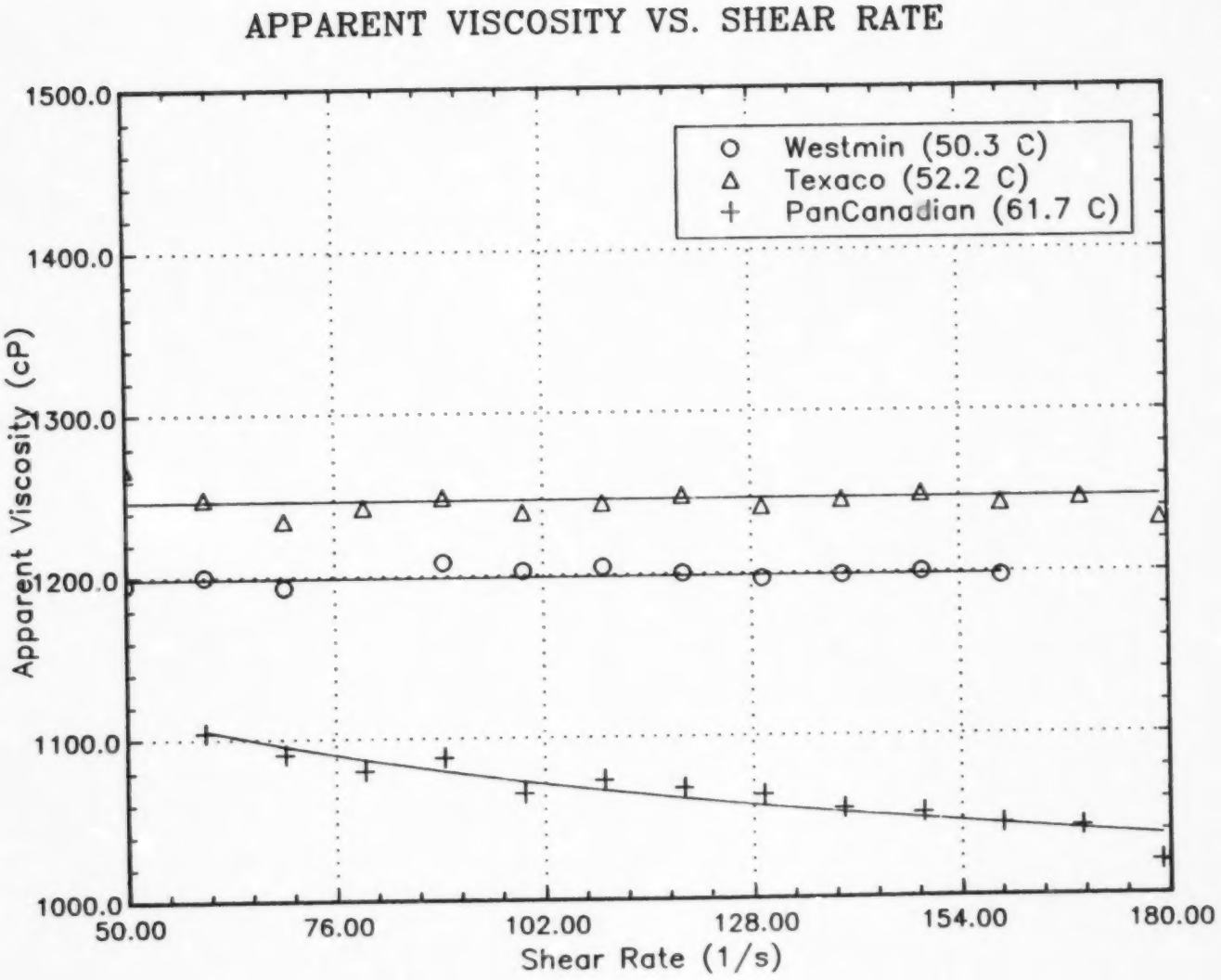
APPARENT VISCOSITY VS. SHEAR RATE
Westmin (50.3 C)
Texaco (52.2 C)
PanCanadian (61.7 C)
Apparent Viscosity (cP)
1500.0
1400.0
1300.0
1200.0
1100.0
1000.0
50.00
76.00
102.00
128.00
154.00
180.00
Shear Rate (1/s)

FIGURE 35

formation. The flow of such emulsions in a porous medium is a complex process. The shear rates involved in the flow of such emulsions toward a production well vary with the distance from the well. Even at a fixed distance, a range of shear rates is involved due to multiplicity of pore sizes present and differences in pore body and pore throat dimensions. In addition the flow through porous medium can change the characteristics of the emulsion by affecting drop size distribution and trapping part of the dispersed phase. This would be especially true when the pore sizes are comparable to the sizes of emulsified water drops.

Currently, the flow of such emulsions through a porous medium is poorly understood. In view of its importance in determining the productivity of thermal heavy oil recovery projects, which more often than not involve emulsions, the need for developing an improved understanding is evident. We need to examine the interactions of various emulsion characteristics and porous medium characteristics in determining the emulsion flow behaviour. This is a formidable task which will require several years of concerted effort. We expect to make a modest start towards this goal in the coming year.

5. CONCLUSIONS AND RECOMMENDATIONS

The following is a summary of what was learned or accomplished during this work.

1. The literature review showed that the rheology of water-in-heavy oil emulsions depends on several factors and is poorly understood.
2. A rheometer for flow curve measurements at elevated temperatures and pressures was made operational.
3. Flow curve measurements, carried out on several emulsions at different temperatures, showed that such emulsions were shear thinning.
4. Deviations from Newtonian behaviour increased with increasing viscosity of the oil and with increasing fraction of water present.

The in situ formation of water-in-oil emulsions can occur in thermal techniques of heavy oil recovery and the flow behaviour of such emulsions through porous media has a direct effect on productivity. Currently it is difficult to mathematically describe the flow of such emulsions through reservoir rocks. There is an urgent need to develop an improved understanding of emulsion flow in porous media.

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